STAT

[redacted]

UNCLASSIFIED

UNITED STATES ATOMIC ENERGY COMMISSION

THEORETICAL PRINCIPLES OF ISOTOPE METHODS FOR INVESTIGATING CHEMICAL REACTIONS

S. Z. Roginsky

Translated by:

CONSULTANTS BUREAU, INC.

Technical Information Service Extension, Oak Ridge, Tenn.

STAT

UNCLASSIFIED

[redacted]

A translation of:

Teoreticheskie Osnovy Izotopnykh Metodov Izucheniya Khimicheskikh Reaktsy S. Z. Roginsky Moskva, Izdatelstvo Akademy Nauk SSSR, 1956, 614 p.

Printed in the U.S.A. Price $2.20. Available from the Office of Technical Services, Department of Commerce, Washington 25, D.C.

ACADEMY OF SCIENCES USSR
INSTITUTE OF PHYSICAL CHEMISTRY

S.Z. ROGINSKY

THEORETICAL PRINCIPLES OF ISOTOPE METHODS FOR INVESTIGATING CHEMICAL REACTIONS

ACADEMY OF SCIENCES USSR PRESS
Moscow, 1956

PREFACE

The postwar development of chemistry has been marked by the rapidly increasing importance of isotopes and isotope methods of investigation. The time has gone when it might have been possible, in a book of moderate size written by one author, to present all the basic information on isotopes and to give an account of their applications in various branches of science or even in different branches of chemistry alone. A characteristic feature of our times is the publication and success of special monographs and symposiums devoted to individual isotopes, and sometimes even to individual compounds, and of an extensive specialized literature on isotope techniques. The position is much less satisfactory with regard to literature on the theory of the unusual phenomena which the laboratory investigator meets when using isotopes in his work.

I have repeatedly found by experience what serious obstacles to the extensive use of isotope methods in chemistry, biology, and technology are presented by an inadequate acquaintance of many research workers with the scientific principles of isotope chemistry and by a lack of books which present them systematically and completely. The research worker who first commences work with isotopes is perplexed by the question of the admissibility of the use of isotopes as tagged atoms when the physical and chemical properties of isotopic compounds are not completely identical. The chemical effects of radiations emitted by radioactive substances often appear to him to offer an insuperable obstacle, and he expects radioactive isotopes to have unusual chemical and biological properties due to instability of their atomic nuclei. Having overcome these apprehensions, the beginner sometimes goes to the other extreme, completely ignoring isotopic corrections when their magnitude is appreciable, and entirely forgetting the chemical effects of radiation. Many disappointments and errors have been caused by neglect of isotopic exchange and inadequate understanding of its mechanism and kinetics.

It is not easy to gain a correct understanding of these matters from the journal literature, as it is very extensive and multilingual. Moreover, many investigations based on statistical thermodynamics and molecular spectroscopy are difficult and insufficiently accessible to the chemist.

A complete utilization of the possibilities of isotope methods in any given field is only possible if they are used in considered conjunction with other methods, and with a thorough understanding of the field of application. The present monograph is essentially centered on the application of isotopes to investigations of the mechanisms of chemical transformations and of the reactivity of substances. Various aspects of this central problem of modern theoretical chemistry are being studied by physical chemists, organic chemists, and technologists. Its status determines to a considerable extent the level of the whole of theoretical chemistry. Therefore a complete utilization of the latent possibilities of isotope methods for investigations of chemical reactions simultaneously requires a good knowledge of certain sections of isotope chemistry and of the theoretical fundamentals of chemical kinetics. Fortunately, we have a rich scientific literature on chemical kinetics, which contains excellent monographs, symposiums, and reviews, and considerable attention is devoted to its theoretical principles in the new teaching courses of physical chemistry and in the latest editions of university text books. A systematic presentation of these principles was therefore considered to be superfluous to this book. General problems of kinetics are touched upon only in direct relation to any actual problems of isotope chemistry under consideration. A few exceptions have been made in the case of problems which have been inadequately treated in our literature on kinetics or which are usually discussed without sufficient attention to features important in relation to the theory of isotope effects. This applies to nucleophilic and electrophilic characteristics of exchange reactions, to the electron mechanism of oxidation-reduction reactions, and to the mechanism and role of tautomeric changes.

Our fundamental ideas of chemical processes have been substantially changed by the discovery of isotopes and their extensive use. Simple and complex individual substances have in most cases proved to be mixtures of substances which, although very similar in properties, are nonetheless different and separable. What had been formerly regarded as a single chemical reaction usually proved to consist of a sum of parallel reactions between molecules differing in chemical composition. Comparisons of physical and physicochemical properties of isotopic substances have revealed and clarified features in the structure of chemical compounds which are very significant in relation to their reactivity. The concept of chemical change itself required radical revision. The discovery of isotopes revealed a new, formerly hidden world of isotope exchange processes, which accompany the usual chemical reactions, but which occur also in total absence of the latter. Isotopic processes are more numerous and varied than elementary processes. At the same time, they are in some respects simpler and more convenient to investigate. For example, complications which hinder measurement of the true rates of "elementary" chemical reactions caused by heat liberation are eliminated. Because of the complete symmetry of the activation barrier, the calculation of absolute rates of reaction is greatly simplified, almost all processes follow the same kinetic law, etc. As, at the same time, all reaction types and mechanisms met among the usual chemical processes are represented in isotope exchange, there is now a natural tendency to use isotope exchange for studying general questions of the mechanism of chemical reactions, their kinetics, and reactivities of substances.

For a long time differences in the rates of chemical reactions of molecules of different isotopic compositions were considered as a complication in work with tracer atoms, which in some instances could be utilized for partial separation of isotopes. The work of recent years has shown convincingly that studies of the magnitudes of kinetic isotope corrections and of the effect of temperature on them can provide valuable and definite indications of the nature of the determining stages of various processes. It is therefore to be expected that in the near future measurement of these corrections will become an integral part of every detailed investigation of chemical reaction mechanisms.

The position of isotope exchange and isotope effects in studies of chemical processes, as outlined above, determined the plan of the present monograph. The following are considered:

1. Thermodynamical isotopic effects and differences in the physical and physicochemical properties of molecules of different isotopic composition (Chapter I and Sections I and II of the Appendix).

2. The kinetics of isotopic exchange in simple and complicated conditions (Chapters II and V).

3. The mechanism of isotopic exchange (Chapter III).

4. Isotope effects in the kinetics of chemical and physicochemical processes (Chapter IV and Section III of the Appendix).

A review and generalization of the results obtained in chemical kinetics with the aid of isotopes, and the prospects for further development of their applications in this direction, could have formed the contents of a separate extensive monograph. However, it seemed wrong to ignore applications completely in "Theoretical Principles," as without some acquaintance with applications a correct evaluation of the level reached by theory cannot be made and the principal tasks which confront the theory cannot be defined. At the same time, such a discussion may prove useful to the reader in selecting effective ways of utilization of the theoretical information in his work. These considerations determined the nature of the final chapter:

5. The principal directions of the use of isotopes in chemical kinetics (Chapter VI).

The position and significance of any given method of investigation in the development of a particular field are determined, on the one hand, by the specific characteristics of the method and its level of development, and on the other, by the theoretical and practical thematics of the field of application. Both these factors vary, and increasingly rapidly for newer methods and more dynamic fields. The role played by the method in the field, and the prospects of further applications, vary accordingly. Despite the very impressive successes in experimental techniques, there are no signs of stabilization in the techniques of work with stable and radioactive isotopes. On the contrary, stimulated by the demands of atomic power and other applications, the development of isotope methods is proceeding at a pace unusual even for the period of "storm and rush" through which the natural sciences are passing. Chemical kinetics as an independent scientific discipline is, in its turn, still very young and in the process of becoming established. Its experimental material is growing at a vast rate, while the theoretical concepts and problems are being continuously modified. While the methods and the field of application are in such a state, the question of the place and prospects of isotope methods in the study of chemical processes cannot be considered from a static viewpoint. For correct orientation it is necessary to detect the principal trends of development and to evaluate as correctly as possible the significance of the different development

directions. In the present state of isotope chemistry and chemical kinetics the validity of the concepts and evaluations given cannot be definitely proved, and only time will show how far they are justified.

In this monograph most attention is devoted to homogeneous processes as the simplest and best understood. Among the heterogeneous reactions, only some of the simplest processes at solid – gas and solid liquid interfaces are considered. It is proposed to consider the laws of isotope displacement and exchange in solid phases, and the main applications of isotopes to heterogeneous catalysis and topochemistry, in another work.

The theory of the phenomena considered in this book was often developed without due regard for the requirements of research workers studying chemical processes. In consequence, a number of questions important in chemical kinetics have been inadequately studied. We have attempted to fill some of these gaps by a new examination of some questions with the use of more convenient methods of theoretical analysis and of new experimental data. This applies, in particular, to the kinetics of complex exchange, the general solutions for which are given apparently for the first time. For greater accessibility, the text includes numerous examples and numerical data, but it was not intended to cover all the enormous experimental material which has accumulated in the journal literature.

The poverty of the literature on isotopes in reference data was the reason for inclusion in the Appendix of tables of thermodynamic functions of isotopic molecules, equilibrium constants for isotopic exchange, and data on kinetic isotopic effects.

As no books or reviews approaching this monograph in character have hitherto been published either in our own or in the foreign literature, gaps and shortcomings in the present work are inevitable, and we will be grateful to have our attention drawn to them by readers. It is to be hoped, however, that even in the present imperfect form "Theoretical Principles" will be useful to people commencing creative work with isotopes, and will assist a further extension of the uses of the latter in research practice.

In conclusion, it is my pleasant duty to thank O.M. Todes and O.V. Krylov, who read the whole book in manuscript form, A.I. Shatenshtein and V.G. Levich, who read individual chapters and offered valuable critical comments and advice, O.M. Vinogradov for active and systematic help with the manuscript, M.A. Elyashevich for discussions of certain questions of molecular spectroscopy, and O.M. Gaisinskaya for aid in compilation of the indexes and tables.

CHAPTER I

THERMODYNAMICAL ISOTOPIC EFFECTS

§ 1. Isotopes and Isotopic Molecules

The fundamental characteristic of any chemical element is its nuclear charge, which coincides with the ordinal number of the element in Mendeleev's periodic table or, which is the same thing, with its Mendeleev number (atomic number) [1]. Atoms of the same atomic number may differ in mass. For example, three types of atoms of atomic number 1, occupying the first space in the table, are known: light hydrogen or protium; stable heavy hydrogen or deuterium; and radioactive heavy hydrogen or tritium; their masses are in the ratio of 1 : 2 : 3.

Ordinary hydrogen contains 99.98% protium and 0.015% deuterium [2], and often also small traces of tritium which come from the atmosphere.

Atoms of the same elements but of different mass are known as isotopes. The possibility of their existence had been suggested by A.M. Butlerov (1881) and W. Crookes (1886). The existence of isotopes is caused by the presence of different numbers of neutrons in the nucleus for a given number of protons.

Atoms of different elements containing the same numbers of nucleons in their nuclei are termed isobars, and atoms of the same isotope, differing in their contents of intranuclear energy and consequently with different radioactive properties, are known as isomers. Of these three terms, the last (isomers) is used in organic chemistry in a totally different sense.

TABLE 1

Examples of Nuclear Isotopes, Isobars, and Isomers

H^1; H^2 (D); H^3 (T)	Isotopes
H^3 (T) & He^3	Isobars
Br^{80}, $\tau_{1/2} = 4.5$ hr. and Br^{80}, $\tau_{1/2} = 18$ min.	Isomers

There is still no generally accepted terminology for designation of the various relationships in molecules differing in isotopic composition or arrangement of isotopes within the molecules; this often leads to confusion. Table 2 illustrates, by actual examples, the system of nomenclature recently proposed by Clusius [4].

It is clear from Table 2 that the most general term, which includes all possible variations of differences in isotopic composition and arrangement of isotopes, is isotopic molecules. It is applicable to molecules differing in isotopic composition of any of the constituent elements, and of several of these elements simultaneously. Isotopic molecules may have different or equal mass numbers. The terms N-isotopic, O-isotopic, S-isotopic indicate for which elements the isotopic composition differs. Isotopic-isomeric molecules differ only by the arrangement of the isotopes within the molecules, i.e., by the isotopic structure and not the isotopic composition. Isotopic-isomeric molecules have the same mass number. If the mass number is the same but the isotopic composition is different, the term isotopic-isobaric molecules is used.

TABLE 2

Types of Isotopic Molecules According to Clusius

Mass number (number of nucleons)	Substance and formula	Group name
	Ethyl alcohol	Isotopic molecules
46	$C_2^{12}H_5OH$	
48	$C_2^{13}H_5OH$	
48	$C^{12}C^{13}H_5OD$	
51	$C_2^{12}D_5OH$	
53	$C_2^{12}D_5O^{18}H$	
57	$C^{13}C^{14}D_5O^{18}D$	
	Phenyl azide	N-isotopic molecules
119	$C_6H_5N^{14}N^{14}N^{14}$	
120	$C_6H_5N^{14}N^{14}N^{15}$	
122	$C_6H_5N^{15}N^{15}N^{15}$	
	Water	O-isotopic molecules
18	H_2O^{16}	
19	H_2O^{17}	
20	H_2O^{18}	
	Nitrous oxide	Isotopic-isomeric molecules
45	$N^{14}N^{15}O^{16}$	
45	$N^{15}N^{14}O^{16}$	
	Toluene	Ditto
94	$C_6^{12}H_5C^{14}H_3$	
94	$C_5^{12}C^{14}H_5C^{12}H_3$	
	Oxygen	Isotopic-isobaric molecules
34	O_2^{17}	
34	$O^{16}O^{18}$	
	Water	Ditto
21	D_2O^{17}	
21	TDO^{16}	
21	HDO^{18}	
21	HTO^{17}	

§ 2. Concept and Examples of Isotopic Exchange

The concept of isotopic exchange unifies processes of very different internal mechanisms. In some instances isotopic exchange involves electron transfer; in others, transfer of atoms or simple monoatomic ions, accompanied by rupture of some chemical bonds and formation of others; in yet others, neutral molecules, complex ions, or radicals are interchanged. Often isotopic exchange of a particular element is induced by ordinary chemical reactions of another element. Finally, there are known instances of isotopic exchange which are caused by transfer of entire molecules without rupture of original or formation of new chemical bonds, i.e., isotopic exchange with- physical processes forming its basis.* With such characteristics of the effect it is not easy to give a terse and strict definition, and most of the formulations met in the scientific literature are applicable only to definite particular types of isotopic exchange. In this book we shall apply the term isotopic exchange to any process, not leading to ordinary chemical or physicochemical changes of a system, which results in a change of isotope distribution between different chemical forms, different phases, or within the molecules. This definition does not restrict isotopic exchange to processes of any definite type or mechanism, but the commonest and most important forms of isotopic exchange are the results of chemical changes of a special kind. Isotopic exchange was unknown in the old, "preisotopic" chemistry, and it does not fit into the usual concept of chemical change. The most typical isotopic exchange reactions do not essentially differ in their inner mechanism in any way from ordinary chemical reactions, but the result of isotopic exchange is not a different distribution of elements within molecules, or between molecules or phases, but a different distribution of isotopes. The definition given is not very illustrative. To make its meaning clearer, we cite a few examples.

Example 1. Isotopic exchange of iron between ferric and ferrous chlorides. We make a mixed solution of ferric chloride containing the radioactive iron isotope Fe^{55} and inactive ferrous chloride. After some time we extract $FeCl_3$ from the solution by means of ethyl ether, and measure its radioactivity. The greater the time that the mixture was left before extraction, the greater will be the decrease in the radioactivity of the ferric chloride and the equivalent increase of the radioactivity remaining in the solution. If the experiment is suffi- ciently long, the radioactivities of the two salts, per atom of iron, will become equal. Ordinary chemical pro- cesses did not occur in the system. The change of activity is the consequence of some special type of process, which can be schematically represented by the equation

$$\left.\begin{array}{l} {}^{55}FeCl_3 + FeCl_2 \rightleftarrows FeCl_3 + {}^{55}FeCl_3, \\ {}^{55}Fe^{3+} + Fe^{2+} \rightleftarrows Fe^{3+} + {}^{55}Fe^{2+}. \end{array}\right\} \qquad (1)$$

This is one of the types of homogeneous isotopic exchange, the mechanism of which is discussed in § 1, Chapter III.

Example 2. Isotopic exchange between potassium iodide and iodine vapor. Vapor of molecular iodine containing an admixture of 8-day iodine radioisotope I^{131} is passed over crystals of potassium iodide containing the only stable iodine isotope of mass number 127. On passing over the potassium iodide, the iodine vapor will give up some of its atoms of the 131 radioisotope, replacing them by an equal number of atoms of the ordinary 127 iodine isotope. In this instance also the process is not accompanied by detectable chemical changes, but the potassium iodide acquires radioactivity which it did not previously have, while the radioactivity of the iodine vapor decreases. This is a consequence of isotopic exchange between iodine 127 and iodine 131. This reaction is heterogeneous; its equation

$$KI^{127} + I^{127}I^{131} \rightleftharpoons KI^{131} + I_2^{127} \qquad (2)$$

represents a heterogeneous chemical process of the isotopic type.

Example 3. Isotopic exchange between liquid mercury and its vapor. On bringing liquid mercury tagged with one of its radioactive isotopes, for example Hg^{203}, into contact with ordinary mercury vapor, it is easy to detect the appearance of radioactivity in the vapor and its decrease in the liquid. This is the result of a heterogeneous isotopic exchange between liquid and vapor, which may be represented as follows:**

---

* A more detailed classification of isotopic exchange based on the nature of the transferred particles is given in § 24, Chapter III

** Of the seven stable mercury isotopes, we have included in Equation (3) the commonest, Hg^{202} (natural occurrence 29.6%) [2].

$$\underset{\text{liquid}}{Hg^{202}} + \underset{\text{vapor}}{Hg^{203}} \rightleftarrows \underset{\text{liquid}}{Hg^{203}} + \underset{\text{vapor}}{Hg^{202}} \qquad (3)$$

In this instance the isotopic exchange is based on evaporation and condensation, i.e., a combination of two physicochemical processes.

In all of these three examples, with far-reaching differences of phase conditions and mechanism of the isotopic exchange, the process involves displacement or change of bond form of individual atoms of the elements concerned. We now cite some examples of isotopic exchange in which not atoms but molecules are exchanged

Example 4. Isotopic exchange of carbon between benzene and its vapor. With the use of benzene tagged with C^{14} or C^{13} it is easy to observe isotopic exchange of carbon between liquid and gaseous, crystalline and gaseous, and liquid and crystalline benzene. It can be shown that in this heterogeneous isotopic exchange no exchange of C atoms or CH groups occurs between different molecules. Only whole C_6H_6 molecules are exchanged, and the mechanism of the isotopic exchange is physicochemical as in Example 3. It should be noted that the same results would be obtained in experiments with hydrogen-tagged benzene with the use of tritium or deuterium.

Example 5. Isotopic exchange of carbon or nitrogen between KCN and $(CN)_2$ and between KCN and HCN.

By tagging the cyanogen carbon or nitrogen in the gas phase, it is possible to bring about the reactions

$$\left.\begin{array}{l} \text{a) } KC^{12}N^{14} + (C^{14}N^{14})(C^{12}N^{14}) \rightarrow KC^{14}N^{14} + (C^{12}N^{14})_2, \\ \text{b) } KC^{12}N^{14} + HC^{14}N^{14} \rightarrow KC^{14}N^{14} + HC^{12}N^{14}; \\ \text{c) } KC^{12}N^{14} + HC^{12}N^{15} \rightarrow KC^{12}N^{15} + HC^{12}N^{14}. \end{array}\right\} \qquad (4)$$

etc.

By our definition, Reactions (4, a) and (4, b) represent isotopic exchange of carbon, and Reaction (4, c), isotopic exchange of nitrogen. However, actually in all three cases the exchange is not between C^{14} and C^{12} or N^{14} and N^{15}, but between $(C^{12}N^{14})^-$ ions or $C^{12}N^{14}$ radicals with $(C^{14}N^{14})^-$, $C^{14}N^{14}$ or $(C^{12}N^{15})^-$ and $C^{12}N^{15}$ ions or radicals respectively The isotopic exchange here is the consequence of exchange between diatomic radicals or ions. Examples of the participation of more complex groups in such exchange can easily be found

Example 6. Isotopic exchange between sulfur dioxide and trioxide. Mixtures of sulfur dioxide with oxygen and sulfur trioxide do not contain either sulfur atoms or SO radicals. However, isotopic exchange between ordinary SO_2 and SO_3 tagged with S^{35} radioactive sulfur proceeds rapidly in presence of Pt, V_2O_5, and other catalysts even in conditions in which, owing to established equilibrium, no apparent chemical reaction occurs. Isotopic sulfur exchange

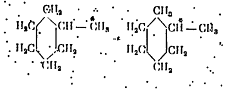
$$S^{32}O_2 + S^{35}O_3 \rightleftarrows S^{35}O_2 + S^{32}O_3 \qquad (5)$$

occurs in consequence of the invisible reversible chemical reaction of oxygen transfer

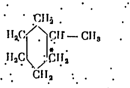
$$\left.\begin{array}{l} S^{32}O_2 + {}^1\!/_2O_2 \xrightarrow{cat} S^{32}O_3; \\ S^{35}O_3 \xrightarrow{cat} S^{35}O_2 + {}^1\!/_2O_2. \end{array}\right\} \qquad (6)$$

The transfer of oxygen atoms is perceived as isotopic sulfur exchange. If in the same system in equilibrium not sulfur but oxygen is tagged, it is possible to observe isotopic exchange of oxygen between $SO^{16}O^{18}$ and SO_3^{16}, based on reversible addition and removal of oxygen.

Example 7. Isotopic exchange of carbon in methylcyclohexane. When methylcyclohexane tagged with C^{14} in the side chain is passed over aluminosilicate catalysts, there is a decrease of the C^{14} content in the methyl group, with its simultaneous appearance in the ring structure. It seems likely that the following reaction occurs:


(7)

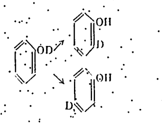
but at the same time



and other isotopic isomers are formed [3].

This is an example of intramolecular isotopic exchange. The next example shows that such exchange is not easy to distinguish from intermolecular exchange.

Example 8. Hydrogen regrouping of phenol. A.I. Brodsky and his associates [24] investigated isotopic isomerization of phenol tagged with deuterium in the hydroxyl group



The process proved to be slow intermolecular exchange with the participation of two molecules.

Apart from isotopic exchange by mechanisms analogous to those illustrated in Examples 1-8, exchange based on combinations of two or more such mechanisms is possible. In particular, electron transfer is often accompanied by transfer of atoms, simple ions, or more complex particles. Transfer of radicals or molecules may be followed by transfer of simple ions and atoms, electron transfer, etc.

Such instances will be met in Chapter III, devoted to the mechanism of isotopic exchange.

§ 3. Isotope Effects

Research workers commencing work with isotopes for the first time are often perplexed by the question of the magnitude of isotope effects, and primarily of the degree of deviation from the normal values of chemical equilibrium constants and rates of chemical processes when particular isotopes of a given element are replaced by others, of different mass and with different nuclear properties. In consequence, doubts arise with regard to the possibility of judging the behavior of elements with the normal isotopic composition by the behavior of isotopes introduced artificially as tagged atoms.

These doubts, like the frequent fear that stable and radioactive isotopes are not chemically equivalent, are without serious basis. The instability of the atomic nucleus, manifested in radioactive disintegration, is associated with the intimate structure of the nucleus, which is in no way reflected in the chemical behavior of the atoms. Neither the valency, nor chemical bond stability, nor reactivity show any practical changes in the transition from an inactive isotope to a radioactive isotope of the same element. Radioactivity will manifest itself only at the moment of disintegration, and the observed radioactive effects occur with complete chemical identity of the original radioactive elements with the ordinary stable atoms of the same elements.* In contrast to the instability of the nucleus, which has no influence whatever on the chemical behavior of the atom up to the instant of its disintegration, the mass and some other properties of the nucleus have a definite, but in the majority of cases very small, influence on the chemical properties.

The differences in the physical and physicochemical properties of isotopes increase with relatively greater differences in the masses of the corresponding isotopes. It is evident that isotope effects should be greatest in the case of hydrogen, in which the masses of the two rare isotopes exceed the mass of the ordinary protium isotope by almost 100% for deuterium (D) and by almost 200% for tritium (T). The mass of radioactive carbon C^{14}, used most frequently as a source of tracer atoms, exceeds the mass of C^{12} by only 16.7%. The differences of the masses of C^{11} and C^{13} from the mass of C^{12} are a half of this (about 8.5%). The isotope effects are correspondingly much less.

The sodium radioactive isotopes Na^{22} and Na^{24} differ from the ordinary Na^{23} isotope in mass by less than 5%, and the radioactive phosphorus isotope P^{32}, by 3% from P^{31}.

For all the heavier elements the differences between the masses of "tagged" and ordinary isotopes do not exceed these values and are often as low as 1% or even less. In such cases the magnitude of the isotope effects is so small that no corrections need be introduced when isotopes are used as tagged atoms. Since in studies of chemical reactions it is more often necessary to deal with molecules composed of light elements hydrogen, carbon, nitrogen, and oxygen – isotope effects cannot be entirely neglected in chemical kinetics, and their magnitude and methods for its calculation require special consideration.

Calculations of isotope effects in chemical thermodynamics and kinetics are based on the statistical theory of chemical equilibria, different formulations and approximations of this theory being used in different cases. We will therefore briefly consider its essential point and examine the magnitude of the corrections which follow from this theory for the equilibrium constants (Chapter I) and absolute rates (Chapter IV) with variations of the isotope composition. Tables are given to show the extent to which the derivations from the statistical theory of isotope effects agree with experimental data.

Various approximations are used in determinations of isotope effects according to the system under consideration and the accuracy with which the problem is to be solved. For isotopes of the heavy elements, zero approximation is often adequate, the chemical properties of isotopic atoms and of molecules differing in isotopic composition being assumed identical. As is known, the discovery of isotopes itself was the result of the discovery by a number of authors [5] of the complete identity of the chemical properties of: a) ionium, corresponding to Th^{230}, and ordinary thorium, consisting of 100% of Th^{232} isotope; and b) radium and mesothorium [6].

We shall term atoms which are completely identical in the chemical sense but which differ in other properties (such as stability of the nucleus) sufficiently to permit separate detection, ideal isotopes. The properties of a molecule should remain unchanged on replacement of some ideal isotopes in it by others. We shall use the term ideal tagged molecules to denote molecules of anomalous isotopic composition and identical chemical properties. Isotopes which are close to being ideal usually differ very little in their physicochemical properties. This is also true for the properties of ordinary and ideal tagged molecules. We shall apply the term ideal isotopic exchange to isotopic exchange with the participation of ideal isotopes and ideal tagged molecules. In the same degree of approximation we can speak of ideal equilibrium of isotopic exchange, the magnitude of ideal isotopic corrections, etc. The above concepts bear the same relation to real isotopic exchange reactions in chemical thermodynamics and kinetics as the concepts of an ideal gas or an ideal solid crystal lattice to real gases and real crystals in molecular physics.

Consideration of general theoretical questions can be suitably commenced with reference to such idealized systems. In the subsequent first approximation the same questions are examined with consideration of the principal effects directly caused by differences of isotope mass. Only in special cases does it become necessary to consider the additional small effects caused by differences in the electronic, magnetic, and other properties of isotopes.

Isotopic corrections can be determined purely by calculation, with the use of general equations which include atomic masses; or they can be derived from determinations of certain physical, primarily spectroscopic constants of the molecules. The second method, which is predominant in statistical thermodynamics, requires extensive initial data and in principle yields the more accurate results. The first method, less accurate but simpler, is often used for calculations of isotopic corrections in chemical kinetics (Chapter IV)

---

* We will not deal here with the chemical action of radiation emitted during radioactive decay, which is the subject of the extensive and rapidly developing radiation chemistry, or with the special properties of the so-called hot atoms which are formed during disintegration.

§ 4. Isotope Effects in Chemical Equilibria

The influence of isotopic composition on chemical equilibrium constants is met both in ordinary chemical reactions and in isotopic exchange. For example, the dissociation constants of deuterium molecules, D_2, or tritium T_2, and of the mixed molecules HD, HT, and DT, differ from the dissociation constant of H_2 (Table 3).*

TABLE 3.

Dissociation Constants of Molecular Hydrogen of Different Isotopic Compositions [7]

T, °K	1000	1500	2000	2500
H_2	$6.45\cdot10^{-18}$	$3.60\cdot10^{-10}$	$2.96\cdot10^{-6}$	$6.92\cdot10^{-4}$
HD	$2.48\cdot10^{-18}$	$1.57\cdot10^{-10}$	$1.36\cdot10^{-6}$	$3.28\cdot10^{-4}$
D_2	$3.71\cdot10^{-18}$	$2.70\cdot10^{-10}$	$2.40\cdot10^{-6}$	$6.17\cdot10^{-4}$
HT	$2.26\cdot10^{-18}$	$1.49\cdot10^{-10}$	$1.32\cdot10^{-6}$	$3.21\cdot10^{-4}$
T_2	$3.01\cdot10^{-18}$	$2.44\cdot10^{-10}$	$2.35\cdot10^{-6}$	$5.94\cdot10^{-4}$

Similar distinctions, although less in magnitude, are found for any other element and for any other reaction, for example, for the formation of acetylene from methane or the dissociation of hydrogen iodide into hydrogen and iodine. Equations (9) and (10) represent these reactions for different isotopic compositions of the original molecules.

$$\left.\begin{aligned} &\text{a)}\ 2C^{14}H_4 \rightleftarrows C_2^{14}H_2 + 3H_2;\\ &\text{b)}\ 2C^{14}D_4 \rightleftarrows C_2^{14}D_2 + 3D_2;\\ &\text{c)}\ 2C^{12}H_4 \rightleftarrows C_2^{12}H_2 + 3H_2;\\ &\text{d)}\ 2C^{12}D_4 \rightleftarrows C_2^{12}D_2 + 3D_2 \end{aligned}\right\} \qquad (9)$$

etc.

$$\left.\begin{aligned} &\text{a)}\ 2HI^{131} \rightleftarrows H_2 + I_2^{131};\\ &\text{b)}\ 2DI^{131} \rightleftarrows D_2 + I_2^{131};\\ &\text{c)}\ 2HI^{127} \rightleftarrows H_2 + I_2^{127};\\ &\text{d)}\ 2DI^{127} \rightleftarrows D_2 + I_2^{127} \end{aligned}\right\} \qquad (10)$$

etc.

Any chemical equilibria involving elements of the usual isotopic composition, and isotopes used as tagged atoms, have different equilibrium constants. In particular, for the equilibria corresponding to Equations (9) and (10),

$$K_a \neq K_b \neq K_c \neq K_d, \qquad (11)$$

where the differences between the constants K_a and K_c and between K_b and K_d respectively are not large; they are considerably less than the differences between K_a and K_b or K_c and K_d.

---

* All the values of equilibrium constants given in the ordinary tables for chemical reactions refer to substances in which all the elements are present in the form of the normal mixtures of natural isotopes.

Not only the equilibrium constants, but the heats of the corresponding reactions, the thermodynamic constants of the reactants, etc., also differ. The rare occurrence of appreciable deviations from a constant isotope composition in elements from different terrestrial sources shows that the thermodynamic constants should change only slightly with variations of isotopic composition, as otherwise appreciable separation of isotopes should often occur in various natural chemical and physicochemical processes.

In view of the magnitude of the isotope effects for hydrogen and of the wide use of deuterium and tritium as tagged atoms, Tables 3 and 20 (pages 12 and 59) give numerical data on the differences found. (See also Appendix). Less complete data are presented also for isotopes of other elements.

Equilibrium constants and heat effects of isotopic exchange can be calculated from the equilibrium constants of suitably chosen elementary chemical reactions.* For example, it is evident that the heat effect of the isotopic exchange

$$D_2 + H_2 \rightarrow 2HD \qquad (12)$$

is equal to the algebraic sum of the heats of dissociation of the three forms of hydrogen molecules participating in the reaction;

$$H_2 \rightarrow 2H;\ D_2 \rightarrow 2D \text{ and } HD \rightarrow H + D; \qquad (13)$$

$$Q_{\text{isot exch.}} = Q_{D_2} + Q_{H_2} - 2Q_{HD} \qquad (14)$$

Similarly, if we know the dissociation constants of ordinary and deuterated hydrogen halides, K_1, K_2, K_3, K_4, etc.

$$\left.\begin{aligned} K_1 &= \frac{[H_2][I_2]}{[HI]^2},\\ K_2 &= \frac{[D_2][I_2]}{[DI]^2};\\ K_3 &= \frac{[H_2][Cl_2]}{[HCl]^2};\\ K_4 &= \frac{[D_2][Cl_2]}{[DCl]^2} \end{aligned}\right\} \qquad (15)$$

etc., then we can easily find from these constants the equilibrium constant for isotopic exchange between ordinary hydrogen iodide and deuterium chloride

$$HI + DCl \rightleftarrows DI + HCl. \qquad (16)$$

Let us derive an expression for the equilibrium constant for Reaction (16). For this, we use the Equations (15) to express [HI], [DI], [HCl], and [DCl] in terms of the molecular concentrations of the corresponding elements and the dissociation constants, for example:

$$[HI] = \frac{[H_2]^{1/2}[I_2]^{1/2}}{K_1^{1/2}}; \qquad [DCl] = \frac{[D_2]^{1/2}[Cl_2]^{1/2}}{K_1^{1/2}} \qquad (17)$$

etc., and substitute these expressions into Equation (18) for the isotopic exchange equilibrium constant

$$K = \frac{[DI][HCl]}{[HI][DCl]} \qquad (18)$$

---

* It is appropriate to extend the term "chemical reaction" to isotope exchange which proceeds by mechanisms characteristic of ordinary chemical reactions. It is then necessary to distinguish between chemical isotopic reactions and chemical elementary reactions. This last term was apparently first introduced by A A Maksimov

This leads to Equation (19), in which the concentration terms vanish and only the dissociation constants remain

$$K = \frac{[D]^{1/2}[I_2]^{1/2}[H_2]^{1/2}[Cl_2]^{1/2} K_1^{1/2} K_4^{1/2}}{K_2^{1/2} K_3^{1/2} [H_2]^{1/2} [I_2]^{1/2} [D_2]^{1/2} [Cl_2]^{1/2}} = \frac{K_1^{1/2} K_4^{1/2}}{K_2^{1/2} K_3^{1/2}} \qquad (19)$$

Isotopic exchange equilibrium constants can also be calculated from the thermodynamic functions for molecules of different isotopic composition, and from certain physical constants of such molecules. We will therefore precede a presentation of the theory of isotopic exchange equilibria by some information on the theory of ordinary equilibria and on the influence of isotopic composition on the physical constants which figure in this theory.

Equilibrium constants can be calculated in various ways. For example, it is possible to use the known relationship between the equilibrium constant and free energy

$$\Delta F = -RT \ln K, \qquad (20)$$

where ΔF is the free energy change in the transition of all the reaction components from unit concentrations to equilibrium concentrations, R is the gas constant, and T is the absolute temperature. K may be calculated from the entropies of the original and final substances, etc. [8]. The dependence of the equilibrium constant on temperature can be calculated from the heat of reaction (Q_v for K_c and Q_p for K_p) from the equation

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2}, \qquad (21)$$

or if Q = constant, in the form

$$K_T = K_0 e^{Q/RT} \qquad (21a)$$

In turn, the dependence of Q on the temperature can be found, by the Kirchhoff equation, from the difference of the heat capacities of the initial and final substances

$$\frac{dQ}{dT} = \Sigma c_i - \Sigma c_j, \qquad (22)$$

where c_i represents the heat capacities of the initial, and c_j of the final, substances [8].

The starting data for calculation of equilibrium constants can be obtained from calorimetric (thermochemical) data or from optical data with the aid of the equations of statistical physics.

For not very complex molecules in the gaseous state the second method is more accurate than the first, and the best recent reference values for K, F, c, etc. have been derived from optical data with the aid of the equations of statistical thermodynamics [9].

§ 5. Statistical Theory of Chemical Equilibria.

At thermal equilibrium, different molecules simultaneously have different contents of internal energy E_{int}, but even with the same value of E_{int} this energy may be differently distributed among different forms of motion. Part of this energy is in the form of the translational energy E_{tr} of the molecule as a whole. For a freely moving molecule E_{tr} can be resolved into components along three Cartesian coordinate axes, and consequently the molecule has three translational degrees of freedom. Part of the internal energy is in the form of vibrations of atoms and groups in the molecule, E_{vibr}. A diatomic molecule has one vibrational degree of freedom. For more complex molecules consisting of n atoms the number of vibrational degrees of freedom, in absence of internal rotation, is $3n - 6$ for non-linear molecules and $3n - 5$ for linear molecules. Each additional degree of freedom of internal rotation (see below) diminishes the number of vibrational degrees of freedom by unity.

Any gas molecule rotates freely as a whole. This rotation corresponds to E_{rot} with two degrees of freedom for linear molecules and three for non-linear. At high temperatures an appreciable part of the internal energy may be present in the form of electron excitation energy E_{el}. A very small part is always present in the form of

the energy of nuclear spin E_{sp}. The internal energy E_{int} of a molecule can, in the first approximation, be represented as the simple sum of all those forms of energy [10].

$$E_{int} = E_{tr} + E_{rot} + E_{vibr} + E_{el} + E_{sp} \qquad (23)$$

At any instant the value of E_{int} and the distribution of internal energy between the individual terms may differ in different molecules of the same kind. The fraction ρ of molecules (having energy E_{int} at equilibrium, and at temperature T) can be expressed as

$$\rho = \frac{n_E}{n_0}, \text{ and } \rho \sim \alpha_i = g_i e^{-E_{i,int}/kT}, \qquad (24)$$

where n_0 is the number of molecules with zero-point energy only (see below), n_E is the number of molecules having energy E_{int}; g_i is the statistical weight of $E_{i,int}$, k is the Boltzmann constant. The value of g_i depends on the distribution of $E_{i,int}$ between the different forms of energy. In the subsequent expressions for selective factors and statistical sums the symbol E will represent the energy both of a single molecule and of N molecules, where N is the Avogadro number.

The principal thermodynamic functions, including equilibrium constants, can be conveniently expressed in terms of Z, the sum of all values of α_i corresponding to different values of E_{int} and its different distributions by forms of motion; this sum for the states of the molecules is

$$Z^0 = \sum g_i e^{-E_i/kT}. \qquad (25)$$

Starting from E = 0, $Z = Z^0 \exp(-E_0/kT)$, where E_0 is the zero-point energy. The state of the system is characterized by the statistical sum Z_s. For an ideal gas containing N molecules, $Z_s = Z^N/N!$

In statistical thermodynamics [9] the following expressions are derived for the principal thermodynamic functions in terms of statistical sums.

The entropy

$$S = R \ln Z_s + RT \frac{\partial \ln Z_s}{\partial T}. \qquad (26)$$

The internal energy

$$E = RT^2 \frac{\partial \ln Z_s}{\partial T}. \qquad (27)$$

From (26) and (27), the free energy is

$$F = E - TS = -RT \ln Z_s. \qquad (28)$$

From Equations (27) and (28), with the use of the known relationships between enthalpy H and internal energy, and between the thermodynamic potential (Gibbs free energy) and Helmholtz free energy respectively

$$H = E + pv, \qquad (29)$$

$$\Phi = F + pv, \qquad (30)$$

it is easy, for substances with a known equation of state, to express H and Φ in terms of statistical sums; for ideal gases pv is replaced by RT.

In numerical calculations and compilation of tables use is often made of the free energy Φ taken from the zero-point energy level $\Phi - E_0$, divided by the absolute temperature. In standard conditions, as used in the theory of gaseous equilibria

$$\frac{-(\Phi - E_0)}{T} = R \ln Z^0/N \qquad (31)$$

In Equations (26) and (27)

$$\frac{d}{dT}\ln Z_s = \frac{1}{RT^2}\frac{\Sigma E_i g_i e^{-E_i/RT}}{\Sigma g_i e^{-E_i/RT}}. \tag{32}$$

Finally, for substances which obey the ideal-gas laws, K for the reaction

$$\nu_A A + \nu_B B + \ldots \rightleftarrows \nu_X X + \nu_Y Y + \ldots$$

may be written in the form of the equation

$$K_s = \frac{Z_X^{\nu_X}\cdot Z_Y^{\nu_Y}}{Z_A^{\nu_A}\cdot Z_B^{\nu_B}} \qquad \text{when } v = 1, \tag{33}$$

which is derived from the equation for the van't Hoff isotherm

$$K_s = \frac{c_X^{\nu_X}\cdot c_Y^{\nu_Y}}{c_A^{\nu_A}\cdot c_B^{\nu_B}} \tag{34}$$

by substitution of the corresponding statistical sums for the concentrations. In a similar manner, heat capacities at constant volume or constant pressure, chemical potentials, etc., may be expressed in terms of statistical sums.

Because of this, solution of the most diverse problems in chemical thermodynamics, including the determination of equilibrium constants for reactions in which isotopes participate and calculations of the isotope correction in the theory of equilibria, reduce to determinations of the numerical values of the statistical sums, or to expression of them in terms of definite physical and physicochemical constants of the substances, followed by substitution of the resultant values and expressions into the equations. An advantage of this method is the direct relationship between Z and quantities which can be determined spectroscopically.

We shall now consider in greater detail the physical meaning of the statistical sum for a complex molecule, the internal energy of which is composed of several terms. According to Equations (23) and (25), the general expression for the statistical sum can be written in the form

$$Z_{\mathrm{int}} = \sum g_i e^{-E_i/kT} = \sum g_i e^{-E_{i\,\mathrm{tr}}/kT}\cdot e^{-E\quad/kT}\, e^{-E_{i\,\mathrm{vibr}}/kT}\, e^{-E_{i\,\mathrm{el}}/kT}\, e^{-E_{i\,\mathrm{sp}}/kT} \tag{35}$$

In the first approximation each of the partial values of E varies independently of the others, and can therefore be regarded as an independent function; Zint can therefore be substituted by the product of the statistical sums for the separate types of energy [9]

$$Z_{\mathrm{int}} = Z_{\mathrm{tr}} Z_{\mathrm{rot}} Z_{\mathrm{vibr}} Z_{\mathrm{el}} Z_{\mathrm{sp}} \tag{36}$$

Each of the partial statistical sums in Equation (36) represents an expression of the form

$$Z_l = g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT} + \ldots = \sum_l g_i e^{-E_i/kT}, \tag{37}$$

where the subscript l indicates the type of energy for which the statistical sum is calculated; E_1, E_2, etc., are the different levels of this form of energy for the molecules of the given substance, and g_1, $g_2 \ldots g_i$ etc., are the statistical weights, or the numbers of different states which correspond to a given value of E for a definite form of internal energy. Consequently, in Equation (35) g_i may be replaced by the product:

$$g_i = g_{i\,\mathrm{tr}}\, g_{i\,\mathrm{rot}}\, g_{i\,\mathrm{el}}\, g_{i\,\mathrm{vibr}}\, g_{i\,\mathrm{sp}} \tag{35a}$$

§6. Statistical Sums for Translational and Rotational Energy

We shall consider separately the values of the statistical sums for different kinds of internal energy. All forms of energy are quantized, i.e., they can assume only certain definite discrete values. For any two energy levels

$$E_{j+1} - E_j = h\nu = hc\omega, \tag{38}$$

where h is the Planck constant; ω is the corresponding characteristic frequency in reciprocal centimeters. The quanta of translational energy are so small that the range of values and corresponding rates of motion can be regarded as continuous. This makes it permissible to replace the statistical sum of Z_{tr} by the integral

$$Z_{\mathrm{tr}} = \sum g_{\mathrm{tr}}\, e^{-E_{\mathrm{tr}}/kT} = \int_0^\infty e^{-E_{\mathrm{tr}}/kT}\, dn, \tag{39}$$

where dn is the number of energy levels in the energy range dE. It is proved in quantum statistics that the energy of translational motion of a particle moving in a cubical box of side a can be expressed for each degree of freedom by the Equation (40)

$$E_{\mathrm{tr}} = \frac{n^2h^2}{8a^2m}, \tag{40}$$

and hence

$$\frac{E_{\mathrm{tr}}}{kT} = \frac{n^2h^3}{8a^2mkT} = n^2\lambda, \tag{41}$$

where, if T = const,

$$\lambda = \frac{h^2}{8a^2mkT} = \mathrm{const}$$

Substituting these values for E_{tr}/kT into Equation (39), we have for each degree of freedom

$$Z_{\mathrm{tr}\ (1)} = \int_0^\infty e^{-n^2\lambda}\, dn = {}^1/_2 \sqrt{\pi/\lambda} = \frac{(2\pi mkT)^{1/2}}{h}a, \tag{42}$$

or, as the complete statistical integral for three degrees of freedom

$$Z_{\mathrm{tr}} = \frac{(2\pi mkT)^{3/2}}{h^3}V, \tag{43}$$

where $V = a^3$, the volume of the cube in question. The result holds for a volume of any shape. In some cases it is convenient to replace V by RT/p.**

The only quantity in Equation (43) to depend on the isotopic composition is the particle mass m, which changes as one isotope is replaced by another. Instead of m we may put the molecular weight M, multiplying the denominator and numerator by $N^{3/2}$, where N is the Avogadro number; this gives

$$Z_{\mathrm{tr}} = \mathrm{const}\cdot M^{3/2}. \tag{43a}$$

For all molecules, with the exception of hydrogen and some of its compounds, the quantum of rotational energy $h\nu_{\mathrm{rot}}$ at not very low temperatures is considerably less than kT ($h\nu \ll kT$). Therefore the rotational spec-

---

* ν in sec^{-1} is the number of vibrations per second. In spectroscopic and thermodynamic calculations vibration frequency is also usually expressed in reciprocal centimeters, and denoted by the symbol ω.

** In Equation (43), Z_{tr} is referred to volume V; Z_{tr}/V represents the translational statistical sum per unit volume.

trium can also be regarded as continuous and in calculations of Z summation can be replaced by integration. Exceptions to this rule in kinetics and catalysis are met only in the ortho–para transformation of molecular hydrogen and in its isotopic exchange at low temperatures.

The statistical weight of a definite rotational level depends both on the rotational quantum number for the corresponding level, and on the spins of the nuclei constituting the molecule, i_1, i_2, etc. This is seen in the fine structure of rotational spectra [10]. Without allowance for the influence of nuclear spin, for a definite rotational quantum number J there are 2J + 1 different orientations with equal energies.

Nuclear spin can introduce a characteristic complication into the system of rotation energy levels of molecules consisting of pairs of similar atoms. In cases in which the nuclear spin is other than zero, instead of one system of levels and a single molecular structure there are two types of structure and two systems of levels, differing in the orientation of the spins of the two nuclei and range of energy levels.

One such structure corresponds to parallel orientation of the spins of the two nuclei and is represented as ↑↑ and the other corresponds to antiparallel orientation and is represented as ↓↑. For one of the nuclear spin orientations in such a molecule quantum statistics permits only odd values of the rotational quantum number J = 1; 3; 5; 7; etc, and for the other, only even values, J = 0; 2; 4, etc. In contrast to asymmetric molecules, for which transitions with changes of J by 1, ΔJ = ± 1, are most probable, for symmetrical molecules of the type in question only ΔJ = ± 2 is possible. For a ΔJ = ± 1 transition, a change of orientation of the nuclear spin in the molecules (↑↑ to ↓↑ and vice versa) is necessary; this does not occur either spontaneously or under the action of radiation. Table 4 gives the values of nuclear spins for a number of atoms.

TABLE 4

Nuclear Spins of Certain Atoms

Element	Mass number of isotope	Nuclear spin in h/2π units	Element	Mass number of isotope	Nuclear spin in h/2π units
Neutron n_0	1	1/2	Fluorine F	19	1/2
Hydrogen H	(p, H) 1 (d, D) 2 (T) 3*	1/2 1 1/2	Phosphorus P	31	1/2
Carbon C	12 13 14*	0 1/2 0	Sulfur S	32 33 34 35* 36	0 3/2 0 3/2 0
Nitrogen N	14 15	1 1/2	Chlorine Cl	35 36* 37	3/2 2 3/2
Oxygen O	16 17 18	0 1/2 0	Bromine Br	79 81	3/2 3/2
			Iodine I	127	5/2

Note: Radioactive isotopes are marked by an asterisk.

It follows from this table that there are two different molecular forms of all symmetrical hydrogen molecules H_2, D_2, and T_2, as well as nitrogen molecules N_2^{14} and N_2^{15}, oxygen O_2^{17}, phosphorus P_2^{31}, sulfur S_2^{33} and S_2^{35}, and the halogens F_2^{19}, Cl_2^{35}, Cl_2^{36}, Cl_2^{37}, Br_2^{79}, Br_2^{81} and I_2^{127}.

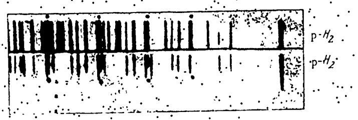


Fig. 1. The hydrogen spectrum [12]. Upper part of figure para hydrogen; lower part – normal hydrogen.

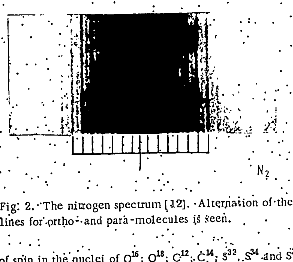


Fig. 2. The nitrogen spectrum [12]. Alternation of the lines for ortho- and para-molecules is seen.

Owing to absence of spin in the nuclei of O^{16}; O^{18}; C^{12}; C^{14}; S^{32}, S^{34} and S^{36} atoms, the molecules O_2^{16}, O_2^{18}, C_2^{12}, C_2^{14}, S_2^{32}, S_2^{34} and S_2^{36} can each exist in only one molecular form. It is customary in spectroscopy to use the term ortho-forms for forms with greater statistical weight, and para-forms for forms with lower statistical weight. For ordinary hydrogen, the odd levels, with parallel orientation of nuclear spins have three times the statistical weight of the even levels with antiparallel spin orientation. Therefore the ↑↑ form with odd values of J = 1,3,5 etc. is termed ortho-hydrogen, and the ↓↑ form with even values of J = 0, 2, 4, para-hydrogen. For nitrogen N_2^{14}, deuterium D_2, and others, the ortho-form is characterized by even quantum numbers, and the para-form by odd quantum numbers, with a 2:1 ratio of statistical weights. Figs. 1 and 2 show the spectra of H_2 and N_2^{14} with clearly defined alternation of more intense lines for the ortho-forms with the weaker lines for the para-forms.

As it is not possible here to deal in greater detail with the theory of these forms, which is excellently presented in Chapter 6 of the first part of the well-known Farkas monograph [11], we will stress only that up to the present, in kinetic and catalytic studies, the existence of ortho- and para-forms in binary molecules of one kind had to be taken into account only in the case of light and heavy hydrogen.

In calculations of statistical sums for monoisotopic molecular hydrogen, it is necessary to calculate their values separately for the ortho- and para-forms, and to find their sum from the contents of each at the given temperature [11] (see also Tables 23, 24). No special ortho- and para-forms exist in binary molecules containing dissimilar nuclei, including HD and HT molecules, and the rotational sum as taken for all integral values of J from 0 to ∞, both even and odd

$$Z_{\text{rot}} = g_{\text{sp}} \sum_{J=0}^{J=\infty} (2J+1)\, e^{-E_J/kT} \qquad (44)$$

In this case, for a binary molecule containing nuclei with spins i and i'

$$g_{\text{sp}} = (2i + 1)(2i' + 1).$$

It is proved in the quantum-mechanical theory of spectra [10, 12] that the rotational energy of a diatomic rigid molecule with moment of inertia I and quantum number J is given by the equation

$$E_{rot} = \frac{J(J+1)h^2}{8\pi^2 I}. \tag{45}$$

Putting $\rho = h^2/8\pi^2 IkT$, substituting the value of E_{rot} into Equation (44), and passing, on the grounds given above, from summation to integration with respect to dJ, we have

$$Z_{rot} = g_{sp} \sum_{J=0}^{J=\infty} (2J+1)\, e^{-\rho J(J+1)} = \tag{46}$$

$$= g_{sp} \int_0^\infty (2J+1)\, e^{-(J+1)J\rho}\, dJ = g_{sp} \int_0^\infty e^{-\rho u}\, du = \frac{g_{sp}}{\rho},$$

where u = (J + 1)J.

Writing in explicit form the values of g_{sp} and ρ, we obtain (47)

$$Z_{rot} = (2i+1)(2i'+1)\frac{8\pi^2 IkT}{h^2}. \tag{47}$$

The moment of inertia of a rigid linear rotator, which may be represented by a rotating dumbbell (Fig. 3), is equal to the product of the reduced mass and the square of the distance r between the centers of atoms 1 and 2.

$$I = \mu r^2. \tag{48}$$

In its turn

$$r \approx r_1 + r_2, \tag{48a}$$

where r_1 and r_2 are the radii of the two corresponding atoms in the molecule, and

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{48b}$$

It is evident from (48b) that μ increases with increasing mass of either atom. If the two values of m are equal,

$$\mu = \frac{m}{2}, \tag{48c}$$

i.e., proportional to m

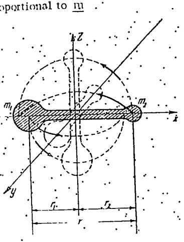


Fig. 3. Rotation of a dumbbell molecule. The broken line shows the positions of the molecule during rotation about one of the axes y and z.

In molecules which differ in isotopic composition only, the values of r are very close to each other. Usually the masses of the atoms also vary little, and therefore variations of I are also not large. The molecules of some hydrogen compounds are exceptions to this.

Table 5 gives values of r, μ, and I for certain substances containing different hydrogen isotopes.

As we pass consecutively from H_2 to D_2 and T_2, the value of μ increases approximately 2 and 3-fold, respectively. The reduced mass of the HT molecule is $\frac{3}{4}$ of m_H or $\frac{3}{2}$ of the reduced mass of H_2. The same sequence of variations of μ is found for compounds of hydrogen with heavier atoms. This is natural, since, for the binary molecules XH, XD, and XT the main part of the sum in the expression for μ^{-1} is the reciprocal mass of the hydrogen isotope:

$$\left.\begin{aligned} \mu_{HX}^{-1} &= \frac{1}{m_X} + \frac{1}{m_H}, \\ \mu_{DX}^{-1} &= \frac{1}{m_X} + \frac{1}{m_D}, \\ \mu_{TX}^{-1} &= \frac{1}{m_X} + \frac{1}{m_T} \end{aligned}\right\} \tag{48d}$$

Since hydrogen is the lightest element, the first term will always be less than the second, and in the limit when $m_X \gg m_T$ we have the ratio

$$\mu_{HX} : \mu_{DX} : \mu_{TX} \approx 1 : 2 : 3. \tag{48e}$$

Table 5 shows clearly that differences in the moments of inertia and in the vibrational and rotational frequencies are also very large.

TABLE 5

Effect of Replacement of H by D and T on Certain Constants of Molecular Hydrogen and its Simplest Compounds*

Molecule	μ, m_H	r, Å	$I \cdot 10^{-41}$, g·cm²	ω_e, cm⁻¹
H_2	0.50	0.7414	4.57	4405.3
DH	0.66	0.7413	6.10	3817.0
D_2	1.00	0.7417	9.15	3118.8
TH	0.75	(0.7414)	6.85	3598.1
T_2	1.50	(0.7414)	13.7	2546.5
OH	0.94	0.9710	14.7	3727.9
OD	1.78	0.969	27.7	2721.2
HCl	0.97	1.2747	25.4	2988.9
DCl	1.89	1.275	51.2	2090.7

---

* The values of r and ω_e are taken from Herzberg's monograph [12]. The values of I are calculated approximately from the formula $I = \mu r^2$. The value of r for TH and T_2 is taken as 0.7414A. ω_e is the fundamental frequency; μ is given in terms of the mass of the protium atom m_H.

For all other elements the differences in μ caused by replacement of one isotope by another are considerably less. Correspondingly, the differences in the values of I and hence the effects of replacement on the magnitude of the rotational sum also become less. This is clear from Equation (47) which, for small values of ρ, is in most cases applicable in the form

$$Z_{rot} = \frac{(2i+1)^2}{2\rho} \tag{47a}$$

also to binary molecules containing two similar atoms. Molecules of H_2, D_2, and T_2 at low temperatures are exceptions.

The figure two in the denominator of Equation (47a) is termed the symmetry factor, σ. This factor indicates the number of indistinguishable identical positions through which a molecule passes during rotation. Many diatomic molecules do not have repeating indistinguishable positions, and σ = 1.

In most of the cases with which we are concerned the electronic levels are not excited, and only g_{el} remains of the sum. Introducing this into the expression for Z_{rot} we have the general expression

$$Z_{rot} = \frac{g_{el}\,g_{sp}}{\sigma}\,\frac{8\pi^2 IkT}{h^2} \qquad (47b)$$

With small changes, which are not considered here, the expression obtained for Z_{rot} is also applicable to linear, tri- and polyatomic molecules. Examples of such molecules are CO_2 and N_2O

For non-linear polyatomic molecules, which have three equal moments of intertia I, and which can be represented by a spherical-rigid rotator (Fig. 4), Z_{rot} is given by Equation (49)

$$Z_{rot} = \frac{g_{el}\,g_{sp}}{\sigma}\,\pi^{1/2}\left(\frac{8\pi^2 IkT}{h^2}\right)^{3/2} \qquad (49)$$

The spherical-rotator model and the corresponding Equation (49) are satisfactorily applicable to many molecules of the type CX_4, including CH_4, CD_4, CT_4, SiX_4 etc. For such molecules the symmetry factor $\sigma = 12$.

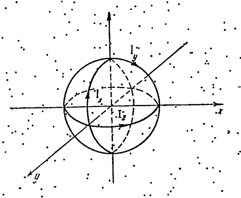


Fig 4 Rotation of a rigid spherical rotator.

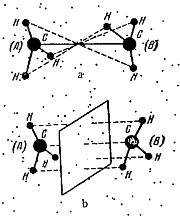


Fig. 5. Structure of a bipyramidal ethane molecule.
a) Trans-form; b) cis-form.

A mechanical model of a molecule with three unequal moments of inertia A, B, and C is an asymmetric top. The expression for Z_{rot} for it has the following form:

$$Z_{rot} = \frac{g_{el}\,g_{sp}}{\sigma}\,\frac{8\pi^2 (8\pi^3 ABC)^{1/2} (kT)^{3/2}}{h^3} \qquad (50)$$

This type includes, among others, benzene and water. Simplified equations have also been derived for certain other models, for example, a symmetrical top with two equal moments of inertia. This model represents fairly well the rotational characteristics of many molecules, among them ammonia and chloroform. In more complex molecules, internal rotations may additionally appear. Thus, the ethane molecule can be represented by the mechanical model of a bipyramid (Fig. 5) in which the two component pyramids, representing CH_3 radicals, rotate about a line joining the carbon vertices, i e., about the C−C bond [13]. Such rotations, predicted long ago by the theory of the structure of organic molecules, involve, in the case of single bonds, the overcoming of very small energy barriers which appear only at very low temperatures. On the other hand, rotation about multiple bonds requires the overcoming of considerable barriers. In large molecules several types of internal rotation may arise.

In the theory of absolute rates of chemical reactions, on which the theory of kinetic isotope effects presented in Chapter IV is based, differences in the values of the rotational sums play a considerable part. These differences, with rare exceptions, have no appreciable influence on isotopic exchange equilibria.

§ 7. Vibrational Statistical Sums

The energy of vibrational quanta considerably exceeds that of rotational quanta. At sufficiently low temperatures only the so-called zero-point energy remains of the vibrational energy of the molecules; at moderate and high temperatures, the vibrational statistical sums introduce considerable corrections into the value of Z_{int}. At sufficiently high temperatures Z_{el} may become very significant.* In isotopic exchange equilibria the deviation of the ratio of the vibrational sums for the original and final substances from unity is one of the main sources of isotopic corrections.

This ratio tends to unity with increase of temperature. The statistical weight of the individual vibrational levels is unity

$$g_{vibr} = 1, \qquad (51)$$

and therefore the expression for the vibrational statistical sum can be schematically written as

$$Z_{vibr} = \sum e^{-E_i\,vibr/kT} \qquad (52)$$

For a diatomic molecule, considered as a harmonic oscillator (Fig. 6), the possible values of the vibrational energy [10, 12] are determined by the equation

$$E_{vibr} = h\nu\,(v + 1/2), \qquad (53)$$

where v is the quantum number which may have any integral value from zero to infinity.

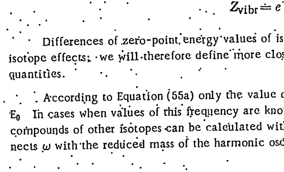


Fig. 6. Potential energy curves for harmonic and anharmonic oscillators. The continuous line above represents the parabolic curve for the potential energy of a harmonic oscillator; the broken line is the curve for an anharmonic oscillator.

By this equation, when v = 0.

$$0 \neq E_{v=0} = 1/2\,h\nu. \qquad (54)$$

This value of E_{vibr}, which is retained when T 0, is termed the zero-point energy [14]

With the use of ω in reciprocal centimeters, Equation (53) becomes

$$E_{vibr} = hc\,(v + 1/2)\,\omega \qquad (55)$$

which at T - 0, when v = 0, becomes

$$E_{vibr} = \frac{1}{2}\,hc\omega. \qquad (55a)$$

Since $E_{0,vibr}$ enters all the terms of the vibrational statistical sum, it can be taken outside the summation sign

$$Z_{vibr} = e^{-E_0/kT} \sum e^{-hcv\omega/kT} \qquad (52a)$$

Differences of zero-point energy values of isotopic molecules play a very significant role in the theory of isotope effects; we will therefore define more closely the meaning of this concept and its relationship to other quantities.

According to Equation (55a) only the value of the fundamental frequency is specific in the expression for E_0. In cases when values of this frequency are known only for a compound of one of the isotopes, its values for compounds of other isotopes can be calculated with satisfactory accuracy by means of Equation (56), which connects ω with the reduced mass of the harmonic oscillator [10, 12].

$$\omega_{i\,vibr} = \frac{1}{2\pi c}\sqrt{\frac{p_i}{\mu}} \qquad (56)$$

where p_i is the force constant for a vibration of the i-th type. Its dimensions are g. sec^{-1} and it depends on the gradient of the potential curve. For molecules differing in isotopic composition only, it is possible, as a first approximation, to equate the values of p_i for all analogous types of vibrations

$$p_i \; p_i^{*} \; p_i^{**} \text{ etc.}$$

---

* For different molecules the temperature regions in which Z_{vibr} begins to influence the thermodynamic characteristics (other than through E_0) are different, and therefore the concepts of low, moderate, and high temperatures are relative. This is also true for Z_{el}.

Because of this, in the same approximation

$$\omega_i^* = \omega_i\sqrt{\frac{\mu_i}{\mu_i^*}} = \omega\gamma_i, \tag{56a}$$

where $\gamma_i = \sqrt{\frac{\mu_i}{\mu_i^*}}$ is the conversion factor for vibrational frequencies of the molecules which appears on change of the isotopic composition. It is evident that these changes are greatest in the transition from protium to tritium and decrease with increasing atomic weights of the elements concerned.

There has been no lack of attempts to calculate ω_i without the use of optical data directly through p_i and μ_i, but as yet caution should be exercised in the use of such calculations for determinations of absolute values of ω. Tables 7 and 20 show values of ω_{vibr} and zero-point energies for certain isotopic molecules. In chemical or physicochemical processes which involve changes of E_0 or the disappearance of one of these quantities, we meet ΔE_0, the change of zero-point energy. Fig. 7 illustrates such changes in the energy scheme of a process.

Since $e^{-E_0/kT}$ is a common factor contained in all the terms of the vibrational sum, it is often preferred to refer the levels not to 0, but to the zero-point energy level, and to use vibrational statistical sums of the type

$$Z^0_{vibr} = \sum_{v=0}^{v=\infty} e^{-hc\omega v/kT}, \tag{57}$$

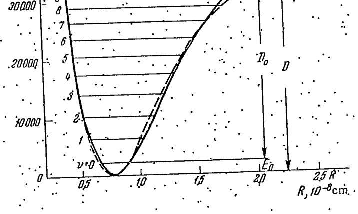


Fig. 7. Diagram of the vibrational levels of linear harmonic and anharmonic oscillators with an indication of zero-point energy levels. The experimental values of the dissociation energy D_0, taken from the zero-point energy level, and the total dissociation energy D, equal to $D_0 + E_0$, are shown.

It is evident that

$$Z_{vibr} = Z^0_{vibr}\, e^{-E_0/kT} = Z^0_{vibr}\, e^{-hc\omega/2kT} \tag{57a}$$

It must be pointed out that in a chemical process the initial states from which the calculations for the statistical sums of the initial and final substances are made, are different, and to reduce them to a common origin, the factor

$$\exp\left(-\frac{E_{0\,init} - E_{0\,final}}{kT}\right) = e^{-Q_0/RT}, \tag{57b}$$

where Q_0 is the heat effect of the process at 0°, is introduced into the corresponding formulas, and in particular into (33), after substitution of Z^0 for Z. For isotopic exchange reactions Q_0 represents the difference between the zero-point energies of the corresponding molecules.

In Equations (55) and (57a), ω is one of the characteristic frequencies of the molecule. Since v can assume any values from 0 to infinity, Z^0_{vibr} in Equation (57) forms an infinite geometrical progression, the denominator $e^{-hc\omega/kT}$ in which is less than unity.

As is known, the sum of the terms of a geometrical progression is

$$\sum = a_0 + a_0Y + a_0Y^2 + \dots = \frac{a_0}{1 - Y}. \tag{58}$$

Since, when v = 0

$$hcv\omega/kT = 0 \text{ and } e^0 = 1, \tag{59}$$

in this instance the first term $a_0 = 1$. Hence

$$Z^0_{vibr} = \sum_{v=0}^{v=\infty} e^{-hc\omega v/kT} = \frac{1}{1 - e^{-hc\omega/kT}}, \tag{60}$$

or

$$Z_{vibr} = \frac{1}{1 - e^{-u}}, \tag{60a}$$

where

$$u = hc\omega/kT. \tag{61}$$

The vibrations of real diatomic molecules are only approximately represented by the harmonic oscillator model. At high vibration amplitudes, i.e., at high v, the deviations become so large that Equation (58) becomes inapplicable. Therefore at very high T, when high vibrational levels are excited, Equations (55) and (60) become inapplicable. The formula

$$E_{vibr} = hc\omega_0(v + \tfrac{1}{2}) - x_0\omega_0(v + \tfrac{1}{2})^2, \tag{62}$$

which includes two terms of the series, is applicable within wider limits. In Equation (62), x_0 is the anharmonicity constant, determined from spectroscopic data. It is inversely proportional to the frequency ω_0 and to the moment of inertia of the molecule.

For exact calculations of thermodynamic quantities further approximations are often used; here the mutual influence of the vibrational and rotational motions of the molecule is taken into consideration, and the vibrational and rotational energies and their spectra are considered jointly [15, 17]. The expression for the energy of a diatomic molecule then assumes the form

$$\begin{aligned} E_{rot\ vibr} = E_0 &+ hc\,[\omega_0 v - x\omega_0 v^2 + y\omega_0 v^3 + \dots] + \\ &+ hc\,\{B_v\,[J\,(J + 1) + \text{const}] + D_v J^2 (J + 1)^2 + \dots\} \end{aligned} \tag{63}$$

In this expression E_0 is the zero-point energy; $hc[\omega_0 v + x\omega_0 v^2 + y\omega_0 v^3 + \dots]$ is the vibrational component and hc$\{B_v[J(J+1) + \text{const}] + D_vJ^2(J+1)^2 + \ldots\}$ is the rotational component of the internal energy [10].

The new coefficients in Equation (63) have the following meaning:

$$\left.\begin{aligned} B_v &= B_0 - \alpha v + \gamma v^2 + \cdots \\ D_v &= D_0 + \beta v + \delta v^2 + \cdots \end{aligned}\right\} \tag{64}$$

In Equation (64)

$$B_0 = \frac{h}{8\pi^2 Ic}; \quad D_0 = \frac{h\omega_0}{4x_0} \tag{65}$$

The terms of the series $-\alpha v + \gamma v^2 + \ldots$ and $\beta v + \delta v^2 + \ldots$ respectively, represent the influence of increasing vibrational energy on the rotational energy. In Formula (63) the term $D_vJ^2(J+1)^2$ and subsequent terms, not [illegible], represent corrections for deviations of a real molecule from the linear rotator model. In turn, the multinomial for the vibrational energy, instead of one correction term for anharmonicity [which figures in Equation (60)] contains an infinite series which is broken off at any suitable term according to the required accuracy and the properties of the system under consideration.

Several approximate equations have been proposed [13-18] for calculation purposes, by means of which it is possible to calculate, to the required degree of accuracy, the values of the combined rotational-vibrational sums, starting with Equations (63) and (64) with substitution of actual numerical results of spectroscopic determinations into the corresponding formulas. These equations are not cited here, as in calculations of small isotopic corrections for values of equilibrium constants, and in calculations of chemical reaction rates, the first approximation is usually regarded as adequate, when Z_{rot} and Z_{vibr} are assumed independent and Equations (47), (49), and (60) are used for them.*

Equation (60) applies to a linear harmonic oscillator. For complex molecules, consisting of n atoms, when n > 3, a total of 3n degrees of freedom must be considered, of which, in absence of internal rotation, 3n − 6 remain for vibrational energy. In theory, this corresponds to 3n − 6 fundamental frequencies, but some of these may coincide. Thus, for instance, for the CO_2 molecule shown schematically in Fig. 8,a, the total number of degrees of freedom is 9. The water molecule (Fig. 8,b) and any other triatomic molecule has the same number of degrees of freedom.

The formula 3n − 6 for the number of vibrational degrees of freedom is valid only for nonlinear molecules. Linear molecules have two instead of three rotational degrees of freedom, and therefore of the total of 3n degrees of freedom, not 3n − 6, but one more (3n − 5) remain for the vibrational energy.

The above calculation of the number of degrees of freedom does not take account of the possibility of torsional vibrations about individual bonds or of free or nearly free rotation about them. Such additional forms of internal motion may introduce appreciable corrections into the values of the thermodynamic functions of organic molecules, including ethane and methanol [12]. Thermodynamic and kinetic isotopic corrections are practically unaffected by internal rotation and torsional vibrations, and the latter are therefore not considered here.

The maximum possible number of "normal" vibrational frequencies of a complex molecule is equal to the number of vibrational degrees of freedom. However, in many cases the experimentally observed number of degrees of freedom is less. This is a consequence of "degeneration" of levels, very common in the energetics and spectroscopy of molecules. Degeneration is coalescence of two or more levels into one. This is accompanied by an increase in the statistical weight of the corresponding states. A typical example of degeneration is seen in the vibrational spectrum of carbon dioxide. According to the formulas 3n − 6 and 3n − 5, the number of vibrational degrees of freedom is three for nonlinear triatomic molecules, and four for linear molecules. Nevertheless, Fig. 8,a for the linear molecule of carbon dioxide shows only three normal fundamental frequencies, which correspond to the three main types of coordinated vibrations of the atoms in the molecules of this gas. The reason for this is the degenerated character of the frequency ω_2 for CO_2, which conceals two types of vibrations, the one shown by arrows in Fig. 8,a, and the other in which analogous vibrations occur in a direction perpendicular to the plane of the figure. In the second case, for example, the central carbon atom can move upward, and the two lateral oxygen atoms simultaneously downward.

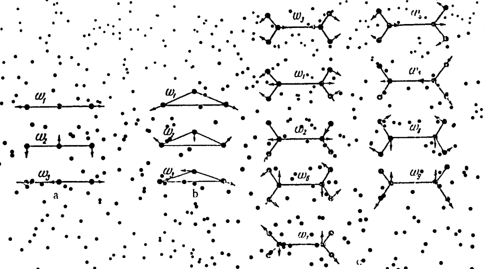


Fig. 8. Types of plane vibrations. a) Linear triatomic molecule (CO_2), b) non-linear triatomic molecule (H_2O); c) plane hexatomic molecule (ethylene) (vibrations perpendicular to the plane of the diagram are omitted).

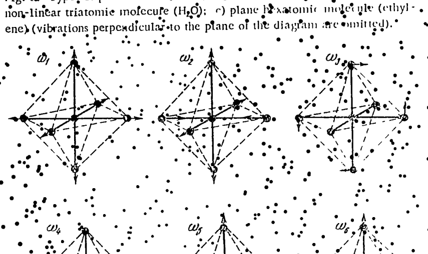


Fig. 9. Types of vibrations. d) Symmetrical spatial molecule (XY_6).

Degeneration is especially pronounced in molecules having a central atom surrounded by several identical peripheral atoms. For example, both methane and carbon tetrachloride, which have a tetrahedral form with a central carbon atom, were each found to have only 4 fundamental frequencies with 9 vibrational degrees of freedom. Of these frequencies, only one is simple, corresponding to fully symmetrical vibrations with simultaneous motion of all four H (or Cl) atoms toward the carbon and away from it. Of the other frequencies one is doubly degenerate, and two are triply degenerate. The existence and nature of degeneration of vibrational levels can often be predicted from the chemical structure of the molecule. More often it is necessary to solve the converse problem — the molecular symmetry and spatial structure is elucidated from the existence and character

---

* Subsequent approximations in Equation (63 - 64) are used in calculations of thermodynamic quantities with the aid of computers. (See § 16 of this chapter and Section 1 of the Appendix.)

of degeneration. Fig. 8, c shows the internal motions of atoms corresponding to nine fundamental plane vibration frequencies of a hexatomic molecule, such as ethylene. The total number of such frequencies is 12, not including the torsional vibration frequencies of the methyl groups.

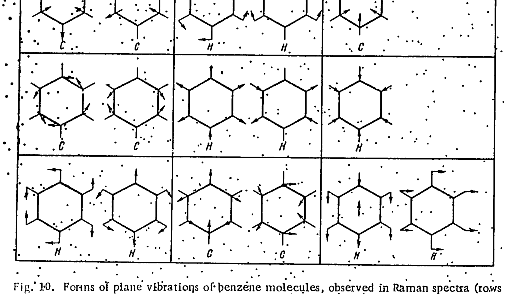


Fig. 10. Forms of plane vibrations of benzene molecules, observed in Raman spectra (rows 1 and 2) and infrared absorption spectra (row 3). Vibrations degenerate relative to each other are shown in the same squares. C) Vibrations of carbon atoms; H) vibrations of hydrogen atoms according to Kohlrausch.

Fig. 9 shows the motions of atoms corresponding to six fundamental frequencies of the SF_6 molecule. Without degeneration, in this case the formula 3n − 6 gives the number of such frequencies to be 15. Finally, Fig. 10 gives a diagram of the spectroscopically observed plane vibrations of the carbon and hydrogen atoms of the benzene ring.

A system of independent harmonic linear oscillators is often used as a model for the vibrations of polyatomic molecules and atoms in crystals. For such a system, with 3n − y oscillators, the vibrational statistical sum is the product Π, which contains 3n − y factors of the form $(1 - e^{-hc\omega_i/kT})^{-1}$, where ω_i is the natural frequency of the i-th type of vibrations (see Figs. 8-10)

$$Z^0_{\text{vibr}} = \prod_{i=1}^{3n-y} (1 - e^{-hc\omega_i/kT})^{-1} = \prod_{i=1}^{3n-y} (1 - e^{-u_i})^{-1}. \tag{66}$$

On the basis of the results obtained for individual partial statistical sums, an approximate expression for the statistical sum of the internal energy of a diatomic molecule of mass m and moment of inertia I can be written in the following form:

$$Z_{\text{int}} = Z_{\text{tr}} \cdot Z_{\text{rot}} = \frac{g_{\text{el}} g_{\text{sp}} (2\pi mkT)^{3/2} \cdot 8\pi^2 IkTe^{-u/2}}{\sigma h^3 h^2 (1 - e^{-u})}, \tag{67}$$

or

$$Z_{\text{int}} = \frac{g_{\text{el}} g_{\text{sp}} 16\sqrt{2}\, \pi^3 \sqrt{\pi} m^{3/2} k^{5/2} T^{5/2} \mu r^2 e^{-u/2}}{\sigma h^5 (1 - e^{-u})}. \tag{67a}$$

Analogous expressions for a linear triatomic molecule or for polyatomic molecules of various forms can easily be derived.

Calculations with the use of Equation (67) and others given in the text are based on measurements of fundamental frequencies, anharmonicity constants, molecular rotation moments, and other coefficients determined from spectroscopic data. Tables 5, 7, 9, and 15 show the influence of variations of isotopic composition on these values. Numerical data for molecules shown in these tables were obtained from band spectra in the visible and ultraviolet regions, from infrared spectra, from Raman spectra, and from microwave spectra at wave lengths of 0.1 to 3 cm. Microwave spectrometry, despite its brief existence, has greatly enriched our information on molecular energy levels, shapes, and dimensions [19]. With its aid it is easy to detect isotope effects in the spectra of compounds of such relatively heavy elements as bromine and selenium, and in principle it is possible to investigate such effects even for compounds of the heaviest elements (lead, mercury, thorium, etc.). It is to be expected that new and effective methods for isotopic analysis of chemical compounds will be developed on this basis in the near future.

§ 8. Fundamental Equations for Isotopic Exchange Equilibrium

We shall now apply the theory discussed in the preceding section to isotopic exchange equilibrium. For clarity, we will begin with the simplest reactions of this type, in which an atom of one isotope replaces an atom of another in a diatomic molecule

$$A\dot{X} + X \rightleftarrows AX + \dot{X}. \tag{68}$$

The equilibrium constant for such a reaction can be written as

$$K = \frac{[AX][\dot{X}]}{[A\dot{X}][X]}. \tag{69}$$

According to the rule stated on page 16, and Equations (33), (52a), and (57a, b) it follows that

$$K = \frac{Z^0_{AX}}{Z^0_{A\dot{X}}} : \frac{Z^0_X}{Z^0_{\dot{X}}} e^{+Q_0/RT} = K_0 e^{+Q_0/RT}\,*, \tag{70}$$

where Q_0 is the heat of the isotopic exchange reaction at absolute zero, per mole.

According to Equation (70), K_0 is a ratio of two fractions. The numerator and denominator of the first contain the statistical sums for diatomic molecules AX, differing in the isotopic composition of X. The second fraction similarly consists of the statistical sums for the X and $\dot{X}$ atoms. Consequently, calculation of K_0 reduces to calculation of two ratios of the statistical sums of molecules differing from each other in isotopic composition only. This general characteristic of isotopic exchange equilibria, applicable to molecules of any degree of complexity, as has been shown by Urey and his associates [20, 21], Bigeleisen and Mayer [22], Tatevsky [23], and others, considerably simplifies calculations of isotopic exchange equilibria [24].

In the given approximation, the statistical sum for a diatomic molecule is the product of the translational, rotational, and vibrational sums. There are no vibrational or rotational sums for free atoms, and at not very high temperatures only the factor g_{el} remains of the electronic sums, and g_{sp} of the nuclear sums

$$\left.\begin{aligned} &\text{a)}\ Z^0_{AX} \cdot Z^0_1 = g_{el} g_{sp} Z_{1\,tr} Z_{1\,rot} Z^0_{1\,vibr} \\ &\text{b)}\ Z_X \approx Z_3 = g_{el} g_{sp} Z_{3\,tr} \end{aligned}\right\} \tag{71}$$

Denoting $Z^0_{A\dot{X}}$ by Z^0_2 and $Z_{\dot{X}}$ by Z_4, we obtain the following expressions for the fractions $\frac{Z^0_{AX}}{Z^0_{A\dot{X}}}$ and $\frac{Z_X}{Z_{\dot{X}}}$:

$$\frac{Z^0_{AX}}{Z^0_{A\dot{X}}} = \frac{Z^0_1}{Z^0_2} = \frac{g_{el\,1}\, g_{sp\,1}\, Z_{1\,tr} Z_{1\,rot} Z^0_{1\,vibr}}{g_{el\,2}\, g_{sp\,2}\, Z_{2\,tr} Z_{2\,rot} Z^0_{2\,vibr}} \tag{72}$$

or

---

* Z^0 is the product $Z^0_{vibr} Z_{tr} Z_{rot}$.

$$\frac{Z_1^0}{Z_2^0}\,\text{ри} = \frac{\sigma_2}{\sigma_1}\,\frac{I_1 M_1^{3/2}(1-e^{-u_2})}{I_2 M_2^{3/2}(1-e^{-u_1})} \qquad (72a)^*$$

For molecules containing one atom of the exchanging isotopes each, the symmetry numbers are equal

$$\sigma_1 = \sigma_2;$$

and therefore we have

$$\frac{Z_1^0}{Z_2^0} = \frac{I_1}{I_2}\left(\frac{M_1}{M_2}\right)^{3/2}\frac{(1-e^{-u_2})}{(1-e^{-u_1})} \qquad (72b)$$

The symmetry numbers which are contained in Z_1^0 and Z_2^0 may also be equal for molecules of the type AX_n in the condition that all the n atoms in the molecule occupy mutually indistinguishable positions, such as the 4 chlorine atoms in CCl_4 or the 6 hydrogen atoms in benzene, and are completely exchanged.

$$CCl_4^{35} \underset{Cl^{35}}{\overset{Cl^{36}}{\rightleftarrows}} CCl_4^{36} \qquad (73)$$

In other cases the ratio $\frac{\sigma_1}{\sigma_2}$ differs from unity and cannot be neglected.

The statistical sum for a free atom with consideration of the electronic and spin factors with nonexcited electronic levels can be written, according to Equation (43), as.

$$Z = \frac{g_{el} g_{sp} (2\pi mkT)^{3/2} V}{h^3} \qquad (74)$$

Hence

$$\frac{Z_X}{Z_X^*} = \frac{Z_3}{Z_4} = \frac{(g_{el} g_{sp})_3 \cdot h^3 (2\pi m_3 kT)^{3/2} V}{(g_{el} g_{sp})_4 \cdot h^3 (2\pi m_4 kT)^{3/2} V} \qquad (74a)$$

Cancelling equal factors in the numerator and denominator, and substituting for the ratio of the masses of the atoms of the two isotopes m_3/m_4 the ratio of their atomic weights M_3/M_4, we have

$$\frac{Z_3}{Z_4} = \frac{g_{sp\,3}}{g_{sp\,4}} \cdot \left(\frac{M_3}{M_4}\right)^{3/2} \qquad (75)$$

The electronic sums also vanish at high temperatures, when the presence of electronically excited atoms cannot be neglected. This is due to the negligible differences in the values of the energy levels and the corresponding frequency differences for all atoms except hydrogen. However, as Table 6 shows, even for hydrogen the effect is not great, since $\Delta\omega$ for the two lines given is only 22.3 and 4.14 cm^{-1}. For He the isotopic shift is approximately an order of magnitude lower and the two values of $\Delta\omega$ given in the table are only 0.85 and 1.40 cm^{-1}. The differences diminish with increasing atomic number. For argon, maximum $\Delta\omega$ = 0.100, etc.

Equating g_{sp3} and g_{sp4}, we have the equation

$$\frac{Z_3}{Z_4} = \left(\frac{M_3}{M_4}\right)^{3/2} \qquad (75a)$$

In the exponent of the last factor of Equation (70) Q_0 may be replaced by the difference of two zero-point energies per mole

$$Q_0 = E_{02} - E_{01}. \qquad (76)$$

Using the connection of E_{02} and E_{01} with ω_2 and ω_1 respectively, and also the possibility of conversion of E/RT into E/kT by division of the numerator and denominator by the Avogadro number N, we have, with the use of the previously introduced contraction $hc\omega/kT = u$,

---

* g_{el} and g_{sp} are omitted in passing from (72) to (72a). In the case of g_{sp} this is justified by $g_{el\,1} \equiv g_{el\,2}$; $g_{sp\,1}/g_{sp\,2}$ in the general case remains.

$$e^{Q_0/RT} = e^{\frac{u_2-u_1}{2}} = \frac{e^{-\frac{u_1}{2}}}{e^{-\frac{u_2}{2}}} \qquad (77)$$

TABLE 6

Comparative Data on Isotopic Displacement in Spectra of Light Elements [26]*

Element	Wave length λ, A	Type of atom	Transition	Isotopes studied	$\Delta\lambda$ exp., A	$\Delta\omega$ exp., cm^{-1}
H	1215.7 6562.8	I I	$1s\,{}^2S - 2p\,{}^2P$ $2p\,{}^2P - 3d\,{}^2D$	$H^1 - H^2$	0.329 1.784	22.300 4.144
He	5015.7 3888.6	I I	$2s\,{}^1S - 3p\,{}^1P$ $2s\,{}^3S - 3p\,{}^3P$	$He^3 - He^4$	0.213 0.212	0.849 1.404
Li	6707.8 5484.7	I II	$2s\,{}^2S - 2p\,{}^2P$ $2s\,{}^3S - 2p\,{}^3P$	$Li^6 - Li^7$	0.160 0.342	0.350 1.14
B	2497.7 3451.4	I II	$2p\,{}^2P_{3/2} - 3s\,{}^2S_{1/2}$ $2s2p\,{}^1P_1 - 2p^2\,{}^1D_2$	$B^{10} - B^{11}$	−0.010 0.104	−0.168 0.877
C	2478.5 2836.7	I II	$2p^2\,{}^1S_0 - 2p3s\,{}^1P_1$ $2s2p^2\,{}^2S_{1/2} - 2s^2 3p\,{}^2P_{3/2}$	$C^{12} - C^{13}$	−0.009 −0.049	0.156 −0.612
N	9629.6 8242.5		$3s\,{}^2P_{3/2} - 3p\,{}^2P_{3/2}$ $3s\,{}^4P_{5/2} - 3p\,{}^4P_{5/2}$	$N^{14} - N^{15}$	0.052 0.041	0.070 0.060
O	8446.4 7157.4 4233.3		$3s\,{}^3S_1 - 3p\,{}^3P_1$ $3s\,{}^1D_2 - 3p\,{}^1D_2$ $4p\,{}^3P_2 - 3d\,{}^3P_2$	$O^{16} - O^{18}$	0.160 0.056 0.084	0.14 0.11 0.47
Ne	7173.9 7032.4 3323.8	I I II	$3p2p_8 - 3s\,1s_2$ $3p2p_{10} - 3s\,1s_5$ $3s\,{}^2P_{3/2} - 3p\,{}^2P_{3/2}$	$Ne^{20} - Ne^{22}$	0.035 0.026 0.029	0.068 0.052 0.260
Mg	2852.1 4571.1 8806.8 2795.5	 I I II	$3s^2\,{}^1S_0 - 3s3p\,{}^1P_1$ $3s^2\,{}^1S_0 - 3s3p\,{}^3P_1$ $3s3p\,{}^1P_1 - 3s3d\,{}^1D_2$ $3s\,{}^2S_{1/2} - 3p\,{}^2P_{3/2}$	$Mg^{24} - Mg^{26}$	0.005 0.017 0.066 0.008	0.061 0.083 0.085 0.102
Cl	4810.1	I	$4s\,{}^5S_2 - 4p\,{}^5P_2$	$Cl^{35} - Cl^{37}$	0.008	0.035
A	7147.0 4510.7 4579.4	 I II	$4s\,{}^1S_5 - 4p\,{}^2P_4$ $4s\,{}^1S_2 - 5p\,{}^3P_5$ $4s\,{}^2P_{1/2} - 4p\,{}^2S_{1/2}$	$A^{36} - Ar^{40}$	0.009 0.010 0.021	0.018 0.048 0.100
K	7699.0		$4s\,{}^2S_{1/2} - 4p\,{}^2P_{1/2}$	$K^{39} - K^{41}$	0.005	0.008

* I refers to neutral, and II to ionized atoms.

Substitution of the expressions obtained for the individual factors in Equation (70) gives Equation (78)

$$K_{\text{isot exch}} = \frac{\sigma_2 I_1}{\sigma_1 I_2}\left(\frac{M_1 M_4}{M_2 M_3}\right)^{3/2} \frac{(1-e^{-u_2})}{(1-e^{-u_1})} \cdot \frac{e^{-\frac{u_1}{2}}}{e^{-\frac{u_2}{2}}} \tag{78}$$

This equation can be simplified further with the aid of Equation (79), which is a special case of the Teller-Redlich spectroscopic theorem [25].*

$$\frac{I_1}{I_2}\left(\frac{M_1}{M_2}\frac{M_4}{M_3}\right)^{3/2}\frac{u_2}{u_1} = 1. \tag{70}$$

Therefore, multiplying and dividing the right hand side of Equation (78) by $\frac{u_2}{u_1}$ we obtain the final Equation (80), in which the only specific constants are σ and u, or, more accurately, ω, which is contained in these functions.

$$K_{\text{isot exch}} = \frac{\sigma^3}{\sigma_1}\frac{u_1}{u_2} \cdot \frac{e^{-\frac{u_1}{2}}}{e^{-\frac{u_2}{2}}} \cdot \frac{(1-e^{-u_2})}{(1-e^{-u_1})} \tag{80}$$

It is to be noted that the same value of K_1 is obtained for the equilibrium in the somewhat more complex isotopic exchange process involving the dissociation of AX and A$\dot{X}$ molecules into atoms

$$\left.\begin{array}{l} AX \rightleftarrows A + X, \\ A\dot{X} \rightleftarrows A + \dot{X}. \end{array}\right\} \tag{68a}$$

Indeed, the equilibrium constants of these two reactions

$$\left.\begin{array}{l} K_{\text{diss}} = \dfrac{[A][X]}{[AX]}; \\ \dot{K}_{\text{diss}} = \dfrac{[A][\dot{X}]}{[A\dot{X}]} \end{array}\right\} \tag{69a}$$

contain the common factor [A], and therefore their ratio is equal to K_1

$$K_1 = \frac{K_{\text{diss}}}{\dot{K}_{\text{diss}}}. \tag{80a}$$

The results obtained for AX are valid for the equilibrium of the isotopic exchange of any tagged diatomic molecule, effected with participation of free atoms according to Equations of the type (68) and (68a), including the reaction

$$B\dot{X} + X \rightleftarrows BX + \dot{X}, \tag{81}$$

effected directly or through two auxiliary equilibria

$$\left.\begin{array}{l} BX \rightleftarrows B + X \\ \text{and} \quad B\dot{X} \rightleftarrows B + \dot{X}. \end{array}\right\} \tag{81a}$$

For K_2 of exchange reaction (81), Equation (80b) should be valid:

$$K_2 = \frac{\sigma_3}{\sigma_4} \cdot \frac{u_3 e^{-\frac{u_3}{2}}}{u_4 e^{-\frac{u_4}{2}}} \cdot \frac{(1-e^{-u_4})}{(1-e^{-u_3})} \tag{80b}$$

This makes it possible to do without moments of inertia and masses in statistical expressions for equilibrium constants for isotopic exchange reactions of any degree of complexity, such as isotopic exchange of diatomic molecules with each other or with complex molecules consisting of larger numbers of atoms.

We shall illustrate this by an example of one of the principal types of exchange found in practice

$$A\dot{X} + BX \rightleftarrows AX + B\dot{X}. \tag{81b}$$

The equilibrium constant K for this reaction may be written as

$$K = \frac{[AX]}{[A\dot{X}]} : \frac{[BX]}{[B\dot{X}]} \tag{82}$$

and at the same time as

$$K = \frac{Z_{AX}}{Z_{A\dot{X}}} : \frac{Z_{BX}}{Z_{B\dot{X}}} = \frac{K_1}{K_2} \tag{82a}$$

With the use of the expressions (80) and (80b) for the equilibrium constants of isotopic exchange between diatomic molecules and atoms, it is easy to write K in a form which does not contain I or M

For this, the reaction (81b) can be represented as the sum of two reactions (83), or, in accordance with the foregoing (page 32), as the sum of four reactions of equilibrium dissociation into A + X; A + $\dot{X}$, B + X, and B + $\dot{X}$.

We shall make use of the first of these possibilities. Evidently,

$$\left.\begin{array}{ll} \text{a)} & A\dot{X} + X \rightarrow AX + \dot{X} \\ \text{b)} & B\dot{X} + X \leftarrow BX + \dot{X} \end{array}\right\} = A\dot{X} + BX \rightarrow AX + B\dot{X}. \tag{83}$$

Assuming that all these partial reactions have gone to equilibrium, we have for reaction (83a)

$$K_1 = \frac{[AX]}{[A\dot{X}]} : \frac{[X]}{[\dot{X}]} \tag{84a}$$

and for reaction (83b)

$$K_2 = \frac{[BX]}{[B\dot{X}]} : \frac{[X]}{[\dot{X}]}, \tag{84b}$$

when K for the isotopic exchange equilibrium of the diatomic molecules A$\dot{X}$ and BX takes the form

$$K = \frac{K_1}{K_2} = \frac{\sigma_2\sigma_4}{\sigma_1\sigma_3}\frac{u_1 e^{-\frac{u_1}{2}}}{u_2 e^{-\frac{u_2}{2}}}\frac{(1-e^{-u_2})}{(1-e^{-u_1})}\frac{u_4 e^{-\frac{u_4}{2}}}{u_3 e^{-\frac{u_3}{2}}}\frac{(1-e^{-u_3})}{(1-e^{-u_4})}. \tag{85}$$

In Equation (85) the subscripts 1 and 2 refer to the molecules AX and A$\dot{X}$, and the subscripts 3 and 4, to the molecules BX and B$\dot{X}$.

The numerators and denominators remaining in the expressions for K_1 and K_2 in Equation (85) are often denoted by Q_1 and Q_2 with subscripts to indicate with which molecule the atoms are exchanged

$$K_1 = \frac{Q_{1A}}{Q_{2A}} \text{ and } K_2 = \frac{Q_{1B}}{Q_{2B}}, \tag{85a}$$

---

* According to the theorem proved in general form by Teller and Redlich, "For two isotopic molecules the product of the ratios $\frac{\dot{\omega}}{\omega}$ for all the vibrations of a given type of symmetry is independent of the potential energy constants, and is determined by the atomic masses and the geometrical structure of the molecule." A mathematical expression of this theorem in general form with examples and limitations is given on page 250 of Herzberg's monograph [12].

where $\frac{Q_1}{Q_2}$ is the ratio of the statistical sums of the ordinary and tagged molecules.

Although, as will be seen from an examination of examples, the presence of numbers of symmetry can lead to considerable deviations of K from 1, a difference in numbers of symmetry cannot in itself result in separation of isotopes: The only result is their different distribution between molecules of different symmetry. Therefore the factors $\frac{\sigma_2}{\sigma_1}$ and σ_4/σ_3 respectively, are often transposed into the left-hand side of the equation; leaving only factors containing u in the right hand side. Then denoting the symmetry numbers of ordinary and tagged molecules by σ_{1y} and σ_{2y}, we have

$$\left.\begin{aligned} \frac{\sigma_1}{\sigma_2}K_A = \frac{\sigma_{1A}}{\sigma_{2A}}K_A = \frac{u_1 e^{-\frac{u_1}{2}}}{u_2 e^{-\frac{u_2}{2}}}\cdot\frac{(1-e^{-u_2})}{(1-e^{-u_1})} = \frac{f(u_1)}{f(u_2)} = f(A\dot{X});\\ \frac{\sigma_3}{\sigma_4}K_B = \frac{\sigma_{1B}}{\sigma_{2B}}K_B = \frac{u_3 e^{-\frac{u_3}{2}}}{u_4 e^{-\frac{u_4}{2}}}\frac{(1-e^{-u_4})}{(1-e^{-u_3})} = \frac{f(u_3)}{f(u_4)} = f(BX) \end{aligned}\right\} \quad (86)$$

$\frac{\sigma_1}{\sigma_2}K_1$ f is often termed the separation coefficient. The fraction in the right hand side of Equation (86) represents the maximum deviation of the isotopes from a state of equal distribution attainable for the given molecules in the simplest exchange reactions with the participation of atoms which by themselves, in view of the classical nature of the statistical sums of translational motion, do not introduce any "separation" factors into isotopic equilibria. The values of the separation coefficients f or, for more complex reactions, the analogous products $\Pi\frac{\sigma_{1i}}{\sigma_{2i}}K_i$ $\Pi f(A_iX)$, serve as the basis for calculations of isotopic equilibria and are often given in tables.

Up to this point, for simplicity, we have confined ourselves to an examination of statistical equations for atoms and diatomic molecules. Equations (87) and (87a) can be used for calculation of equilibrium constants for exchange with atoms and the corresponding separation coefficients for complex molecules consisting of three or more atoms:

$$K = \frac{Q_{1\,(RX)}}{Q_{2\,(R\dot{X})}} = \frac{\sigma_2}{\sigma_1}\prod_i\left[\frac{u_{1i}e^{-\frac{u_{1i}}{2}}}{u_{2i}e^{-\frac{u_{1i}}{2}}}\frac{(1-e^{-u_{2i}})}{(1-e^{-u_{1i}})}\right]; \quad (87)$$

$$f = \frac{\sigma_1}{\sigma^2}K = \prod_i\left[\frac{u_{1i}e^{-\frac{u_{1i}}{2}}}{u_{2i}e^{-\frac{u_{2i}}{2}}}\frac{(1-e^{-u_{2i}})}{(1-e^{-u_{1i}})}\right]. \quad (87a)$$

In this equation $\prod_i$ is the product of all the fractions with different natural frequencies ω_i in the exponent $u = hc\omega/kT$. The subscripts 1 and 2 refer to molecules with different isotopic compositions.

For isotopic exchange between molecules, which follows the more complex Equation (88)

$$aA\dot{X} + bBX \rightleftarrows aAX + bB\dot{X}. \quad (88)$$

the equilibrium constant assumes the form

$$K = \left(\frac{Q_{1A}}{Q_{2A}}\right)^a : \left(\frac{Q_{1B}}{Q_{2B}}\right)^b = K_1^a/K_2^b. \quad (89)$$

The separation coefficient, as previously, will be represented by equations of the type (87a) with corresponding removal of the ratios $\frac{\sigma_{1A}}{\sigma_{2A}}$ and $\frac{\sigma_{1B}}{\sigma_{2B}}$ raised to powers a and b. Equations of this type form the basis of all calculations for equilibrium constants of isotopic exchange.

Determinations of the magnitude of isotope effects in chemical equilibria are important for precise evaluation of the equilibrium distribution of isotopes between individual chemical species and for evaluation of the maximum possible separation effects based on chemical equilibria. This distribution is the limit to which any isotopic exchange reaction tends. It is therefore necessary to become acquainted with methods for numerical

calculation of isotopic exchange equilibria and isotopic corrections for ordinary equilibrium constants. In numerical calculations of these quantities special approximations must be used for equilibria involving hydrogen isotopes. This is primarily due to the considerable absolute and relative changes of the vibrational frequencies $\Delta\omega_i$ and $\Delta\omega_i/\omega_i$, and the reduced energies Δu_i and $\Delta u_i/u_i$ when one hydrogen isotope is replaced by another. Moreover, the rotational spectrum of molecular hydrogen cannot be regarded as continuous (classical) even at room temperature. Therefore it is necessary, for all isotopic equilibria with the participation of molecular forms of hydrogen to calculate or determine from experimental data the values of the rotational sums in explicit form.

§ 9. The Bigeleisen–Mayer and Tatevsky Approximate Equations and Functions

The Equations (80), (85), (86), (87a), and (89) derived above for K and f form the calculation basis for isotopic exchange reactions of all elements except hydrogen.

Of the factors which characterize the energy spectrum of a molecule, these equations contain only values of $u_i = h\omega_i c/kT$, which may be regarded as reduced temperatures

$$u_i = \frac{\theta_i}{T}, \quad (90)$$

where

$$\theta_i = \frac{h\omega_i c}{k} \quad (90a)$$

is the characteristic temperature of the i-th vibration; or as values, reduced to kT units, of the energy differences between adjacent vibrational levels of the harmonic oscillator

$$u_i = \frac{\Delta E_i}{kT} \quad (91)$$

where

$$\Delta E_i = hc\omega_i = h\nu.$$

For further transformations of Equations (87) and (87a) it is necessary to define the sign of the difference between the values of u_i for analogous vibrations of two isotopic forms.

As was noted earlier, on page 23, the frequency ω and therefore the reduced energy u of the vibrational frequencies, increase with decreasing atomic weight of the isotope. We will denote by a prime the values of these quantities u_i' and ω_i' for the lighter of the compared isotopes, writing them without primes for u_i and ω_i for the heavier isotope. With these designations we have, in the subsequent equations

$$u_i' = u_i + \Delta u_i \quad (92)$$

and

$$\omega_i' = \omega_i + \Delta\omega_i. \quad (92a)$$

The signs of Δu_i and $\Delta\omega_i$ are always positive

$$\Delta u_i > 0 \text{ and } \Delta\omega_i > 0. \quad (93)$$

For all elements except hydrogen the relative magnitudes of changes of Δu_i and $\Delta\omega_i$, $\frac{\Delta u_i}{u_i}$ and $\frac{\Delta\omega_i}{\omega_i}$ are very small. The values of $\Delta E_i = hc\omega_i$ are also small in comparison with kT, and therefore $\Delta u_i \ll 1$ (of the order of 0.001-0.01). It is therefore permissible, replacing u_i' by $u_i + \Delta u_i'$ in the equation for K and f, to reduce them to a form which is readily simplified. We do this for the function

$$f = \frac{Q_1}{Q_2} = \frac{\sigma_1}{\sigma_2}K.$$

Let us consider the equilibrium for the case in which Q_1 of Equation (87) corresponds to the heavier, and Q_2 to the lighter isotope. Then, in Equation (87a), u_{1i} becomes u_i, and u_{2i} becomes $u_i' = u_i + \Delta u_i$, and the expression for f takes the form

$$f = \prod_i \frac{u_i}{u_i + \Delta u_i} e^{\frac{\Delta u_i}{2}} \frac{1 - e^{-(u_i + \Delta u_i)}}{1 - e^{-u_i}} \tag{94}$$

We write the first factor in the form

$$\frac{1}{1 + \frac{\Delta u_i}{u_i}} = \frac{1}{1 + \delta} \tag{95}$$

where $\delta \ll 1$. The function $\frac{1}{1 + x}$ represents the sum of an infinite geometrical progression with alternating signs, with first term $a = 1$ and denominator $\varphi = -x$. It can therefore be written [27] as

$$\frac{1}{1 + x} = 1 - x + x^2 - x^3 + \cdots \tag{95a}$$

since $x = \delta \ll 1$, all the terms of the series except the first two can be neglected, and we can write

$$\frac{u_i}{u_i + \Delta u_i} = \frac{1}{1 + \frac{\Delta u_i}{u_i}} = 1 - \frac{\Delta u_i}{u_i} \tag{95b}$$

e^x can be resolved into a series [26] as follows

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \cdots \tag{96}$$

Since $\frac{\Delta u_i}{2} \ll 1$, taking $\frac{\Delta u_i}{2} = x$, in this series we can confine ourselves to two terms

$$e^{\frac{\Delta u_i}{2}} = 1 + \frac{\Delta u_i}{2} \tag{96a}$$

The fraction $\frac{1 - e^{-(u_i + \Delta u_i)}}{1 - e^{-u_i}}$ can be multiplied by $\frac{e^{u_i}}{e^{u_i}}$ to give

$$\frac{e^{u_i} - e^{-\Delta u_i}}{e^{u_i} - 1} \tag{97}$$

Taking $\Delta u_i = x$, we resolve $e^{-\Delta u_i}$ into a series according to the formula

$$e^{-x} = 1 - \frac{x}{1!} + \frac{x^2}{2!} - \cdots \tag{97a}$$

and taking only the first two terms in this case also, because of the smallness of Δu_i, we have

$$\frac{1 - e^{-(u_i + \Delta u_i)}}{1 - e^{-u_i}} = \frac{e^{u_i} - 1 + \Delta u_i}{e^{u_i} - 1} = 1 + \frac{\Delta u_i}{e^{u_i} - 1} \tag{97b}$$

Multiplication of (95b) by (96a) and (97b) converts (94) into (98)

$$f = \prod_i \left(1 - \frac{\Delta u_i}{u_i}\right)\left(1 + \frac{\Delta u_i}{2}\right)\left(1 + \frac{\Delta u_i}{e^{u_i} - 1}\right), \tag{98}$$

which, after it has been multiplied out and terms of the second and third order have been neglected, takes the form

$$f = \prod_i \left[1 + \left(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1}\right) \Delta u_i\right]. \tag{98a}$$

It is easily seen that i-fold multiplication with rejection of terms containing small quantities of second and higher powers converts the product (98a) into a sum (98b)

$$f = 1 + \sum\left(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1}\right)\Delta u_i = 1 + \delta. \tag{98b}$$

This simple formula, first derived by Bigeleisen and Mayer [22] for separation coefficients, has also proved very convenient for calculations of equilibria. A characteristic feature of this formula is that it contains, as a multiplying factor, the function

$$G = \frac{1}{2} - \frac{1}{u} + \frac{1}{e^u - 1} \tag{99}$$

This function is represented in G and u coordinates in Fig. 11. Table 1 (appendix) gives values of G for values of u between 0 and 25.

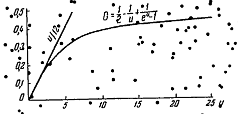


Fig. 11. The complete function G(u) and its approximate expression u/12, after Bigeleisen and Mayer

According to Equation (87), the same function determines the value of $K = \frac{\sigma_2}{\sigma_1} f = \frac{\sigma}{\sigma'} f$* and, because of the known relationship between F and ln K, also the difference of the free energies of formation of two isotopic molecules. It is easy to show that

$$\Delta F^0 - \Delta F'^0 = -RT \ln K = -RT \sum_i G_i \Delta u_i + RT \ln \frac{\sigma}{\sigma'} \tag{100}$$

Hence, with the use of the known thermodynamic formulas, it is possible to obtain a number of approximate expressions also for other thermodynamic characteristics of isotopic exchange.

Further simplifications of the Formulas (98b) and (100) are possible at small values of u_i. In this case the procedure used in simplification of Equation (87a) leads to

$$f = 1 + \sum_i \frac{\Delta u_i \cdot u_i}{12} = 1 + \sum \frac{\Delta (u_i^2)}{24} \tag{101}$$

In Fig. 11 the straight line passing through the origin represents the function $\frac{u}{12}$ which replaces G in Equation (101) in this new approximation.

It is clear from the figure that these two functions practically coincide approximately up to u = 2. At u = 4, the deviation already reaches about 25% and continues to increase with increasing u

The Bigeleisen – Mayer equation is not the only one to be used for calculations of separation coefficients and equilibrium constants. However, it is more convenient than most others for practical purposes. Table 2 in the Appendix gives the values of other thermodynamic quantities calculated with the aid of the function G(u) for different values of u. One interesting peculiarity of the result obtained must be pointed out. It is clear from Fig. 11 that G is positive for any value.

Since in the convention used Δu_i is also positive, the separation function f is always greater than unity. This means that both in dissociation and in exchange of atoms the heavier isotope is retained more firmly than the light in the molecule, and accumulates in it.

At low temperatures and high frequencies ω_i, the function G approaches $^1/_2$. The free energy difference $\Delta F^0 - \Delta F^{0\prime}$ in Equation (100) tends to $-RT\frac{\Delta u_i}{2}$. Since $\frac{Nhc\omega_i}{2}$ represents the zero-point energy E_0 per mole at a temperature which tends to 0, $\Delta F^0 - \Delta F^{0\prime}$ in turn tends to the difference of the zero-point energies ΔE_0

At sufficiently high temperatures Equation (101) is valid for all vibrations, and since both Δu_i and u_i contain T in the denominator, the equation

---

* $\frac{\sigma_2}{\sigma_1}$ is substituted by $\frac{\sigma}{\sigma'}$, and u_{1i} and u_{i2} are substituted by u_i' and u_i.

$$f = 1 + \frac{\gamma}{T^2} \tag{101a}$$

should be valid.

Equation (101a) shows how the separation function f tends to 1 with increase of temperature. It is clear from Equation (101a) that with a sufficiently large temperature increase separation of isotopes based on differences of thermodynamic properties becomes impossible, as does also the utilization of isotope effects in equilibria. Real isotopes show the same behavior as ideal isotopes, identical in the thermodynamic sense and not separable by exchange reactions. In practice, the ideal state is reached at temperatures which decrease with decreasing difference of the frequencies of natural vibrations in the isotopic molecules.

An inconvenient characteristic of the Formulas (98) and (101) derived above is the need to determine all the partial values of ω_i. In this connection we note the possibility of a useful simplification in cases of isotopic exchange of central atoms of symmetrical complexes, the peripheral atoms of which are similar, but are present in different numbers. For example, in the reaction

$$Si^{28}F_4 + Si^{30}F_6 \rightleftharpoons Si^{30}F_4 + Si^{28}F_6 \tag{102}$$

the number of peripheral atoms n = 4 for SiF_4 and n = 6 for SiF_6. In such cases it is sufficient for molecules of each type to determine one frequency ω_i, corresponding to vibration in the direction of the bonds linking the peripheral to the central atoms, and f is approximated as

$$f = \left(1 + \frac{\Delta M}{24M^2} u_1^2 n\right) \frac{\sigma'}{\sigma} \tag{103}$$

Of the other approximate equations for calculation of isotopic equilibrium constants, we will examine those derived by V. M. Tatevsky [28a]. It appears that this work was performed at the same time as that of Bigeleisen and Mayer, but was published in full only in 1951 [28b].

Tatevsky calculates the equilibrium constant for a reaction of the type

$$\nu_1 A + \nu_2 \mathring{B} + \ldots \rightleftharpoons \nu_1 \mathring{A} + \nu_2 B + \ldots,$$

from the generally accepted statistical expression

$$K = \left(\frac{Z_{\mathring{A}}}{Z_A}\right)^{\nu_1} \cdot \left(\frac{Z_B}{Z_{\mathring{B}}}\right)^{\nu_2} \tag{104}$$

As in the approximate solutions by other authors, each of the statistical sums Z_A, Z_B, etc., is considered as the product of the statistical sums of the main forms of motion for a given substance without allowance for the interaction of vibrations with rotations, i. e., without correction for anharmonicity

$$Z = Z_{tr} Z_{rot} Z_{vibr} Z_{el} \tag{105}$$

The usual expressions given in § 5-7 are used for each of the partial statistical sums. The peculiarity of the work lies in the method of simplification of the general expression for the ratio of the vibrational sums of the i-th vibration $(1 - e^{-hc\omega_i/kT})^{-1}/(1 - e^{-hc\omega'_i/kT})^{-1}$, multiplied by the factors $e^{-hc\omega_i/2kT}$ which allow for zero-point energies. For isotopic molecules this ratio is replaced by the ratio of fundamental frequencies, $\frac{\omega'_i}{\omega_i}$, which is denoted by $1/r_i$.

$$f_i = \frac{e^{-hc\omega'_i/2kT}\,(1 - e^{-hc\omega_i/kT})}{e^{-hc\omega_i/2kT}\,(1 - e^{-hc\omega'_i/kT})} \approx \frac{\omega_i}{\omega'_i} = \frac{1}{r_i}$$

This leads to the following approximate value of the part of the equilibrium constant containing the vibrational sums:

$$K_{vibr} = \prod_{i=1}^{n_A} \left(\frac{\omega_{i\mathring{A}}}{\omega'_{iA}}\right)^{\nu_1} \cdots \prod_{i=1}^{n_B} \left(\frac{\omega'_{iB}}{\omega_{i\mathring{B}}}\right)^{\nu_2} \tag{106}$$

The usual expressions for the rotational and translational sums are then used to obtain, with the aid of the Redlich theorem, the already familiar expression for the equilibrium constant

$$K = \left(\frac{\sigma_A}{\sigma_{\mathring{A}}}\right)^{\nu_1} \cdots \left(\frac{\sigma_{\mathring{B}}}{\sigma_B}\right)^{\nu_2} \tag{107}$$

which includes only the symmetry numbers σ_A, $\sigma_{\mathring{A}}$, σ_B and $\sigma_{\mathring{B}}$ and the stoichiometric coefficients ν_1 and ν_2. Examples of the good applicability of this equation, which we have already met, to high-temperature equilibria are instructive. Thus, for example, the values of K_{vibr} given in Table 8 are obtained for hydrogen exchange equilibria between differently substituted deuteromethanes, based on the fundamental frequencies given in Table 7.

TABLE 7

Fundamental Frequencies for $CH_\alpha D_\beta$ ($\alpha + \beta = 4$) According to Tatevsky (Degeneration of Individual Frequencies Shown in Parentheses)

CH_4	CH_3D	CH_2D_2	CH_3D	CD_4
2915	2983	2139	2141	2085
1306	1156	1082	1046	996
3020	3031	3013	2263	2258
3020 (2)	2205 (2)	2227	3015 (2)	2258 (2)
		2974		
1306 (2)	1307 (2)	1286	1988 (2)	996 (2)
		1033		
1520 (2)	1477 (2)	1424	1295 (2)	1054 (2)

TABLE 8

Equilibria of Deuterium Exchange in Methanes (K_{vibr}) at 1000°K, $\frac{\omega_{max}}{T} \approx 3$ (after Tatevsky).

Reaction	K_{vibr} from exact equation	K_{vibr} by (106)	Error, %	K_p by (107)
$CH_4 + CH_2D_2 \rightleftarrows 2CH_3D$	0.837	0.910	−8.7	8/3
$CD_4 + CH_2D_2 \rightleftarrows 2CHD_3$	0.785	0.855	+9.0	8/3
$CH_4 + CHD_3 \rightleftarrows CH_3D + CH_2D_2$	0.958	0.923	−3 7	6
$CH_3D + CHD_3 \rightleftarrows 2CH_2D_2$	1.119	1.015	−9 3	9/4
$CH_4 + CD_4 \rightleftarrows 2CH_2D_2$	0.805	0.801	−0.5	36
$CH_4 + CD_4 \rightleftarrows CH_3D + CHD_3$	0.754	0.790	+4.8	16
Mean absolute error	—	—	6.0	—

This table clearly shows the magnitude of the errors which this approximation involves at 1000°K. The error diminishes with increase of temperature and increases with rise of temperature. For cases in which the zero-point energy cannot be neglected, the author gives more complex forms of the original expression, replacing it by the equations

$$f_i = \left(\frac{1}{r_i}\right)^{1+\mu_i} = \frac{\omega_i}{\omega_i'}\left(\frac{\omega_i}{\omega_i'}\right)^{\mu_i} \tag{108}$$

or

$$f_i = \frac{\omega_i}{\omega_i'}\gamma_i\left(\frac{\omega_i'}{\omega_i}, \frac{\omega_i}{T}\right) \tag{109}$$

In these equations

$$\mu_i = \varkappa\left(\frac{\omega_i}{T}\right)^{\nu},$$

and ν is a constant the meaning of which is not defined. It is easy to see that K' and K" calculated from Equation (108) and (109) are connected with K by the equations

$$K' = K\prod_{i=1}^{n_A}\left(\frac{\omega_{iA}}{\omega_{iA}'}\right)^{\mu_i\nu_i}\prod_{i=1}^{n_B}\left(\frac{\omega_{iB}}{\omega_{iB}'}\right)^{\mu_i\nu_i} \tag{110}$$

and

$$K'' = K\prod_{i=1}^{n_A}(\gamma_{iA})^{\nu_i}\prod_{i=1}^{n_B}(\gamma_{iB})^{-\nu_i} \tag{111}$$

The author gives a table of values of the function γ_i for various values of r_i and $\frac{\omega_i}{T}$ and calculates the percentage error which results from the use of Equation (110) for calculation of f_i. It appears that a fair degree of accuracy can be obtained in this way, but the practical value of the second approximation and of the function γ_i are not clear from the paper, especially as the expressions used are close to being exact in their complexity. It is also not clear whether calculations by means of these equations have any advantage over calculations by the simpler and verified equations of Bigeleisen and Mayor.

§ 10. Isotopic Equilibria of Carbon

For the research worker using isotope methods in kinetic and catalytic studies great interest attaches to isotopic exchange equilibria with the participation of carbon isotopes C^{12}, C^{13}, and C^{14}, and also to some extent C^{11}.

Table 9 gives optical constants of certain carbon compounds, which are used for calculation of separation coefficients and equilibrium constants. In addition to the fundamental frequencies ω_0, used for calculation of f_i and Δu; the table also gives the products $\omega_0 x_0$ used in the next approximation, which takes account of anharmonicity. As a rule this product enters the equation with the (−) sign. The principal data in the table are based on the paper by Urey [21], who used Herzberg's monograph [12], and have been checked against the latest edition of Landolt-Börnstein [29].

At first Urey and Greiff [30], using spectroscopic data, calculated separation coefficients for a number of compounds and isotopic exchange equilibrium constants for certain reactions. In a later review which took into account subsequent publications by a number of authors, Urey [21] gives tables of data calculated by means of Equations (70) and (78). The resolution into series used by Urey in these papers for the conventional statistical sum of the isotopic molecules (or, more precisely, for the equilibrium constants of their isotopic exchange reactions with the participation of free atoms) differs somewhat from the more convenient Bigeleisen-Mayer method described above. The calculation accuracy is approximately the same in both cases, but Urey's results, being the earlier, have been used in later publications by other authors, and his tables may be regarded as generally accepted.

The upper portion of Table 10, separated by a line, includes values of Q_2/Q_1 for a number of carbon compounds, i.e., in our notation the values of K from Equations (85), (85a), and (87). The value of $Q_2/Q_1 = K$ coincides with the separation coefficient $\underline{I}$ of Equation (86) to the accuracy of the ratio of the symmetry numbers. The values for each compound are given for five temperatures (273.1; 298.1; 400; 500 and 600° on the absolute scale) apart from the ∞ value at 0°K. The data for $\frac{C^{13}}{C^{12}}$ in Table 10 represent the ratio Q_2/Q_1 for diamond

The lower portion of the table has a different meaning. This is no longer K for the imaginary auxiliary exchange reaction between molecules and free atoms, but for an isotropic exchange reaction between different chemical substances, for example $HC^{13}N$ and $C^{12}N^-$, or $C^{13}O$ and C^{12}. For each pair of isotropic molecules shown on the left in the form of the fraction $\frac{\overset{*}{A}X}{AX}$, the table shows, for absolute zero and five different temperatures, the values of isotropic exchange equilibrium constants with six compounds, represented in the form of the fraction $\frac{\overset{*}{B}X}{BX}$ at the top of the table. To avoid repetition in this form of "two-dimensional graph" (comparable to chess tournament tables) of reciprocal values of K, half the spaces (under the diagonal) have been left empty. The designations are so chosen that the greatly predominating values of K > 1 represent accumulation of the heavy isotope. The values of equilibrium constants for 15 exchange reactions of C^{13} with C^{12} are shown, after substraction of exchange with own atoms, which in this notation gives K = 1. For all these reactions at all temperatures, except 0°K, K > 1. The only exceptions are two values of K at 500 and 600° for exchange of $C^{13}O_3^{2-}$ with $C^{12}O_2$. In agreement with theory, for all the reactions in Table 10 deviations of K from unity are greatest at the lowest temperature, 273.1°, and least at 600°K. However, even the highest value of K only reaches 1.126, that is, it exceeds by only 12.6% the value of the constant for ideal isotopic exchange. Most of the equilibrium constants in Table 10 are lower, not reaching even 1.1. These figures represent the theoretical separation capacity, i.e., the theoretical enrichment factors of the corresponding reactions.

TABLE 9

Frequencies and Anharmonic Terms for Certain Carbon Compounds [21]:

I. Diatomic molecules

Molecule	ω_0, cm^{-1}	$-\omega_0 x_0$, cm^{-1}	Molecule	ω_0, cm^{-1}
$C^{12}O^{16}$	2167.4	13.28	$C^{12}N^{14-}$	2080
$C^{13}O^{16}$	2119.2	12.69	$C^{13}N^{14-}$	2036.17
$C^{12}O^{18}$	2115.2	12.65	$C^{12}N^{15-}$	2047 76

II: Triatomic molecules

Molecule	ω_i	x_{ij}		Molecule	ω_i	x_{ij}		Note
CO_2	1351.20	— 0.3	+ 5.7	HCN	2000.6	+52 0	— 4.2	Column 2 gives in parentheses the degree of degeneration of the level. Data in Columns 3 and 4 represent two anharmonicity coefficients.
	672.20 (2)	— 1.3	—21.9		729 3 (2)	— 2 85	—14 40	
	2396.40	—12.5	—11.0		3451.5	—55.48	—19 53	
$C^{13}O_2$	1351.20	— 0.30	+ 5,54	$HC^{13}N$	1996 63	+50.25	— 4 09	
	653.12 (2)	— 1.23	—21.28		722 96 (2)	— 2 80	—14 09	
	2328.40	—11.80	—10.38		3435.38	—54 96	—19 27	
CO_2^{18}	1273.92	— 0.27	+ 5.29	HCN^{15}	1968 63	+50 36	— 4.13	
	661.94 (2)	— 1.26	—20.33		728.22 (2)	— 2 84	—14.17	
	2359.81	—12.1	—10.07		3450 86	—55.46	—19,50	

The exchange equilibrium constants for gaseous C^{12} and C^{13} atoms, given in the upper part of the table, are somewhat higher, reaching 1.2358 or 24% for CO_3^{2-} at 273 1°K. However, such reactions can become real only at very high temperatures, when all K = 1. Since, conversely, at absolute zero all values of K tend to infinity, a decrease of temperature below 0°C raises the theoretical separation coefficients.

The data in Table 10 give a correct idea of isotopic equilibria in reactions used for separation of carbon isotopes. More complex molecules are usually met in catalysis and kinetics. In such cases definite selection of fundamental frequencies is often difficult, and such frequencies may be determined by complex coordinated

TABLE 10

Isotopic carbon exchange

	$\frac{C^{13}O_3^{2-}}{C^{12}O_3^{2-}}$	$\frac{C^{13}O_2}{C^{12}O_2}$	$\frac{C^{13}}{C^{12}}$	$\frac{HC^{13}N}{HC^{12}N}$	$\frac{C^{13}O}{C^{12}O}$	$\frac{C^{13}N^-}{C^{12}N^-}$	T, °K
Q_2/Q_1	1.2358 1.2057 1.1274 1.0870 1.0629	1.2169 1.1909 1.1233 1.0877 1.0656	1.2081 1.1786 1.1077 1.0722 1.0516	1.1358 1.1206 1.0802 1.0581 1.0441	1.1086 1.0970 1.0659 1.0479 1.0360	1.0980 1.0875 1.0589 1.0427 1.0323	273.1 298.1 400 500 600

Isopic exchange separation functions

$\frac{C^{13}O_3^{2-}}{C^{12}O_3^{2-}}$	1.000 — — — —	1.016 1.012 1.004 0.999_4 0.997_4	1.023 1.023 1.018 1.014 1.011	∞ 1.088 1.076 1.045 1.027 1.018	∞ 1.115 1.099 1.058 1.037 1.026	∞ 1.126 1.109 1.066 1.042 1.030	0 273.1 298.1 400 500 600
$\frac{C^{13}O_2}{C^{12}O_2}$	— — — — —	1.000 — — — —	1.007 1.010 1.014 1.014 1.013	∞ 1.071 1.063 1.040 1.028 1.021	∞ 1.098 1.086 1.055 1.038 1.029	∞ 1.108 1.095 1.061 1.043 1.032	0 273.1 298.1 400 500 600
$\frac{C^{13}}{C^{12}}$	— —		1.000 — — —	∞ 1.064 1.052 0.025 1.013 1.007	∞ 1.090 1.074 1.039 1.023 1.015	∞ 1.100 1.084 1.046 1.028 1.017	0 273.1 298.1 400 500 600
$\frac{HC^{13}N}{HC^{12}N}$	— —	— — — —	— —	1.000 — — — —	∞ 1.025 1.022 1.013 1.010 1.008	∞ 1.034 1.030 1.020 1.015 1.011	0 273.1 298.1 400 500 600
$\frac{C^{13}O}{C^{12}O}$	— — — — —	— — — — —	— — — — —	— — — — —	1.000 — — — —	∞ 1.010 1.009 1.007 1.005 1.004	0 273.1 298.1 400 500 600

vibrations of several or many atoms. If the fundamental frequencies for the bonds broken and formed in the reaction are known, it is sufficient to find ω_i only for bonds directly participating in the isotopic exchange. Because of the approximate additivity of the force constants and bond rupture energies in a complex molecule, and the approximate proportionality of ω_i to the square root of the bond rupture energy

$$\omega_i \approx \sqrt{D}$$

the natural frequency values for each type of bond vary within fairly narrow limits; for example: for C–H from 2900 to 3310 cm^{-1}, and for C–N from 1033 to 1150 cm^{-1}. A high degree of accuracy in determination of ω is not required for evaluation of the possible corrections for the isotopic effect in work with tagged atoms and in calculations of separation coefficients. In fact, an error of n% in the value of u will result in the same change in the value of $\Delta u = u' - u = u\sqrt{\frac{\mu_1}{\mu_2}} - u = u\left(\sqrt{\frac{\mu_1}{\mu_2}} - 1\right)$ in Equation (98b) and similar equations.

At the same time it is clear from Fig. 11 that with the smallest values of u an error of n% will change the value of G by the same percentage. At moderate and high values of u the relative change of G will be less. Consequently, the maximum value of the correction term δ in the expression f [illegible] 1 + δ is reached at small values of u. As the result of summation of the errors for G and Δu_i it is equal to [illegible]n%. At high values of u the error in the determination of Δδ is n%. The range of values of ω for a given bond type is not wide; even for CH it is only 10%. For C–C, C–N, etc., the differences are much less. In the most typical cases δ is a few hundredths or 1-2 tenths; and therefore in most cases values of δ to an accuracy of 10-20% are adequate. Rounded-off values of ω ensure this with a large margin. Therefore, instead of exact individual values of ω for a given bond type in each compound, with the exception of bonds including hydrogen, it should be possible to use rounded-off typical values, for example ω = 990 cm^{-1} for C–C bonds or ω = [illegible]150 cm^{-1} for C–N bonds (Table 11).

As Table 11 shows, for the three most important single bond types not containing H in organic chemistry, ω differs only by ±2% from the average value of 1010. For double bonds between carbon and nitrogen and oxygen, deviations from average values of ω = 1680 lie between ±1.5 and ±4%, etc. For hydrogen bonds, not only the absolute range of ω, but also the deviations are greater.

In exact calculations of ordinary chemical equilibrium constants the use of group and average values of $\bar{\omega}$ is inadmissible. On the other hand, such an approximation is legitimate for evaluation of the errors introduced into applications of tagged molecules by deviations of the equilibrium distribution of isotopes from equipartition, and also for calculations, which are by their nature highly inaccurate, of separation coefficients in systems far from ideality [28]. For approximate estimates it is possible to use the cruder method of replacing the average values of ω for individual bond types such as C–N, etc., by average group values for several bonds (Table 12). Thus, according to V.N. Kondratyev, ω lies in the range of 800-1200 cm^{-1} for all bonds in organic molecules of the type X–Y, where both X and Y can be C, N, S, or O. This range is wider than Hibben's, owing to the use of the maximum possible differences, and not differences between average values for the bonds.

It is clear from Table 13 that deviations from the mean for different bond types lie between 20% for X–Y and 9% for X≡Y. The errors are usually less than 11%. It is easy to show, however, that even errors of this order in the value of ω have little effect on the value of K if a correct ratio of ω_i' and ω_i, i.e., a correct relative magnitude of isotopic displacement of the vibrational frequencies is retained. This is clear from Equation (99). Therefore this approximation is quite suitable for problems met in the use of tagged molecules.

V.M. Tatevsky [31] has given useful equations for calculation of unknown vibrational frequencies of molecules from known vibrational frequencies of molecules isotopic with them.

Returning to Table 9, we note that the fluctuations in the values of the force constants within a group of related bonds, in accordance with theory, are approximately double the fluctuations of ω.

Thus, from (56a)

$$\bar{\omega} = \omega_0\sqrt{p}$$

or, for the ratio of two values of ω

$$\frac{\omega'}{\omega} = \frac{\omega + \Delta\omega}{\omega} = 1 + \frac{\Delta\omega}{\omega} = \sqrt{1 + \frac{\Delta p}{p}}, \qquad (112)$$

or, since $\frac{\Delta p}{p} \ll 1$,

$$\sqrt{1 + \frac{\Delta p}{p}} \approx 1 + \frac{\Delta p}{2p} \qquad (113)$$

and

$$\frac{\Delta\omega}{\omega} = \frac{1}{2}\frac{\Delta p}{p}. \tag{114}$$

Confirmation of these relationships by the data of Table 11 verifies the applicability of the harmonic oscillator model to the bonds in question even in complex molecules.

TABLE 11

Frequencies and Valency Force Constants for Different Bond Types Without Allowance for Isotope Effects, after Hibben [31].

Bond	Frequency, ω, cm^{-1}	$p \cdot 10^{-5}$ dyne · cm^{-1}	Note
C — C	993 $\bar{\omega} = 1010$	4.64	For harmonically oscillating diatomic molecule
C — O	1030	5.00	
C — N	1033	4.85	
C — S	650	2.14	
C = C	1620 $\bar{\omega} = 1680$	10.60	$\omega = 4.125\sqrt{\frac{p}{\mu}}$, where $\mu_a = \frac{m_1 \cdot m_2}{m_1 + m_2} \cdot N$
C = O	1700	11.60	
C = N	1650	10.40	
C ≡ C	2120 $\bar{\omega} = 2160$	15.82	
C ≡ N	2150	17.50	
C ≡ O	2146	18.50	
N ≡ O	2224	20.90	
C — H atom	3050	5.02	
N — H	3370	6.20	
O — H	3650	6.80	
H — H	4158	5.05	
Cl — H	2880	4.75	
Br — H	2558	3.80	
I — H	2572	3.78	

TABLE 12

Range of Fundamental Vibration Frequencies for Groups of Chemical Bonds in Organic Molecules, after V.N. Kondratyev [10]

Bond	ω, cm^{-1}	Bond	ω, cm^{-1}	Bond	ω, cm^{-1}
X — Y	800—1200	X — Cl	650—750	X — H	2570—3400
X = Y	1500—1810	X — Br	550—600		
X ≡ Y	2000—2400	X — I	500—520	X — D	2000—2500

We will note two more factors significant in a correct evaluation of the isotope effects for carbon.

1) Since C^{11}, like C^{13}, differs from C^{12} by one unit of mass, isotope effects in C^{12}/C^{11} exchange equilibria should be of almost exactly the same magnitude as in C^{13}/C^{12} equilibria. However, the corrections will be opposite in sign, i.e., in the exchange of C^{11} with C^{12} the former will accumulate in compounds which become poorer in C^{13}, and conversely.

2) All the effects for C^{14} will be of the same sign as for C^{13}, but they should be approximately double in magnitude. It is to be noted that the examples of the deviations of K from unity shown in Table 10 give a correct idea of the magnitude of isotope effects for C^{14} in exchange of carbon isotopes between organic molecules, which are most often met in catalysis and kinetics, and which are usually more complex and heavier than the small inorganic molecules and ions shown in Table 10.

TABLE 13

Range of Deviation of Frequencies from the Mean for Different Bond Types

Bond	$\bar{\omega}$	$\Delta\omega$	$\frac{\Delta\omega}{\bar{\omega}}$	Bond	$\bar{\omega}$	$\Delta\omega$	$\frac{\Delta\omega}{\bar{\omega}}$
X — Y	1000	±200	0.2	X — Cl	700	±50	0.07
X = Y	1650	±150	0.09	X — Br	575	±25	0.04
X ≡ Y	2200	±200	0.09	X — I	510	±10	0.02
				X — H	3300	±400	0.12

For a correct estimate of the possible influence of the isotope effects on the results obtained in work with compounds of radioactive carbon isotopes and C^{13}, used as tagged molecules, it should be noted that deviations from equipartition of the isotopes at equilibrium, caused by atomic weight differences, are in most cases far greater than the degree of accuracy in determinations of radioactive isotopes attainable with counters and counting schemes in the usual methods. Similarly, the detection of concentration differences of weight isotopes of the order of a few per cent is a difficult problem. Therefore corrections for separation need only be introduced in the most exact tracer work. Such corrections may become considerable for cumulative isotope effects.

§ 11. Isotopic Equilibria of Other Elements (N, O, etc.)

We will now consider the possible deviations from equipartition in isotopic exchange equilibria for nitrogen, oxygen and certain other elements. It is clear from Table 4 that, for the elements considered below, the nuclear spins of isotopes used in tracer studies are usually not zero. This should lead to the existence of ortho- and para-forms in N_2^{14}; N_2^{15}; F_2^{19}; Cl_2^{35} and a number of other monoisotopic diatomic molecules. However, the distances between the rotational quantum levels for all these molecules are so small that, in all the temperature range of interest for kinetic investigations, the rotational statistical sums can be treated by the classical procedure, with the use of the corresponding integrals without separation of the rotational levels into even and odd. This is also the case for C^{13}, which has spin differing from zero; this was not mentioned earlier, as C_2 molecules can be met as separate particles only in the very high temperature region. We may mention the spectrum of C_2 in hot flames [32] in which all isotopic separation effects vanish completely owing to the high temperature.*

Table 4 of the Appendix gives Urey's data [21] on isotopic exchange equilibria of nitrogen.

This table shows, in the same notation system as is used in Table 10, and for the same five temperatures, calculated values of Q_2/Q_1 for molecular nitrogen and five of its compounds, and also the equilibrium constants for all the fifteen separate isotopic exchange reactions which can take place between these forms of nitrogen. The table shows that for the exchange of N^{14} with N^{15} the deviations of the equilibrium constants from unity are of the same order as for C^{13}/C^{12}. The maximum values of K do not exceed 1.04, and these are reached only in a few reactions with the participation of NH_4^+ at 273.1°. Even at this temperature K reaches only 1.062 for NO/CN^- and HCN/CN^- exchange.

The only oxygen compound of nitrogen given in Table 1 of the Appendix is nitric oxide. Spindel [35] has recently made careful calculations of certain gaseous equilibria of isotopic exchange of nitrogen in its oxygen compounds. Table 14 is taken from his paper.

---

*According to the most recent mass spectrum data, the vapor of evaporating graphite consists predominantly of C_3 molecules, and contains much less C_2 and C_1 [33], [34]. The concentration of C_5^+ is unexpectedly high.

TABLE 14

Equilibrium Constants for Exchange of N^{15} and N^{14} Nitrogen Isotopes at 25°C, after Spindel [35]

	$\frac{N^{15}O_3^-}{N^{14}O_3^-}$	$\frac{N^{15}O_2}{N^{14}O_2}$	$\frac{N^{15}O_2^-}{N^{14}O_2^-}$	$\frac{N^{15}O}{N^{14}O}$	Note
Q_2/Q_1	1.16_9	1.10_9	1.07_2	1.06_0	The last digit, not claimed to be accurate by the author, is printed below the others.
$N^{15}O_3^-/N^{14}O_3^-$	(1.00)	1.05_3	1.09_0	1.09_6	
$N^{15}O_2/N^{14}O_2$	—	(1.00)	1.03_4	1.04_0	
$N^{15}O_2^-/N^{14}O_2^-$	—	—	(1.00)	1.00_6	
$N^{15}O/N^{14}O$	—	—	—	(1.00)	

TABLE 15

Fundamental Frequencies of Isotopic Oxygen Compounds of N^{14} and N^{15}, after Spindel

Molecules*	ω_1	ω_2	ω_3	ω_4
$N^{14}O^{16}$	1906.54			
$N^{15}O^{16}$	1872.34			
$N^{14}O_2^{16}$	1320	648	1621	
$N^{15}O_2^{16}$	1313	636	1587	
$(N^{15}O_2^{16})$**	[1296.4]	[644.3]	[1587]	
$N^{14}O_3^{16-}$	1050	831	1300 (2)	720 (2)
$N^{15}O_3^{16-}$	1050	809.3	1351.9 (2)	720 (2)
$N^{14}O_2^{16-}$	1320	750	1220	
$N^{15}O_2^{16-}$	1304.51	741.16	1198.93	

The degree of degeneration is shown in parentheses.

---

* The NO molecule is satisfactorily represented by a harmonic oscillator with one frequency ν; NO_2^- is represented by an equilateral triangle; NO_2 is also non-linear; NO_3^- has the form of an equilateral triangle with nitrogen in the center. The Appendix gives Urey's table for isotopic oxygen exchange (Table 2).

** Data from various sources are given for $N^{15}O_2^{16}$.

For use in independent calculations, Table 15 also gives values of the fundamental frequencies of isotopic molecules, used and calculated by Spindel.

The data in Table 14 show that in this case also the isotopic corrections are of the same order of magnitude. Even at 0°C they reach only a few per cent, while at 327°C (600°K) the greatest correction is only 2%. For some systems the corrections represent only tenths of one per cent, while in some individual cases small isotope effects of reverse sign are found.

To draw correct general conclusions concerning the magnitude and sign of isotopic corrections for equilibrium constants it is necessary to remember that, after hydrogen, C, N, and O are the lightest elements taking part in isotopic exchange in the use of tagged atoms and molecules. For heavier elements — P, S, Cl, Br, As, etc. — the isotopic corrections are generally still less. Individual data on isotope effects for these elements are given in Table 40, §19.

§12. Isotope Effects in Adsorption

a) Experimental data

The adsorption of atoms is influenced by their zero-point energy of bonding with the solid surface, and

therefore K should differ for different isotopes. This is also true for molecules differing in isotopic composition. The simplest method of adsorptional enrichment of isotopes was described by Glueckauf and his associates [36]. They found K = 1.021 for Ne^{20} and Ne^{22} neon isotopes on active carbon at −194°. In this case the adsorption was purely physical, of the dispersion type. In the same investigation the separation of Li^6 and Li^7 isotopes on an ion exchange resin from lithium acetate solution was studied. The adsorption consisted of displacement of Na^+ and H^+ of the original adsorbent by lithium ions. In this case the equilibrium constant for the separation was 1.022. With a carefully selected procedure for operation of the column it proved possible to obtain a small amount of pure Li^7. In passing, we will note the original method used for analysis. To determine the Li^6 and Li^7 contents, the sample was irradiated with slow neutrons, inducing in Li^6 (but not in Li^7) the nuclear reaction

$$^6_3Li + ^1_0n \rightarrow ^7_3Li^* \rightarrow ^4_2He + ^3_1H + 4 \text{ Mev} \qquad (115)$$

The intensity of emission of heavy ionizing particles (He and T) was used as a measure of the Li^6 content. The values of K found by Glueckauf et al. practically coincide with the values obtained earlier for lithium isotopes by Taylor and Urey [37] with the use of inorganic zeolite adsorbents. The values of K for neon and lithium correspond to the reactions

$$\left.\begin{array}{c} Ne^{22} + Ne^{20}\text{ ads.} \rightleftharpoons Ne^{20} + Ne^{22}\text{ ads.}, \\ Li^6 + Li^7\text{ ads.} \rightleftharpoons Li^7 + Li^6\text{ ads.} \end{array}\right\} \qquad (116)$$

In the first case, the heavier isotope is concentrated on the adsorbent, and in the second, the lighter. According to Taylor and Urey, in adsorption on zeolites, the heavier isotope accumulates from a mixture of K^{39} and K^{41} potassium isotopes. In ion exchange adsorption of ammonium ions, the $N^{15}H_4^+$ ion accumulates on the zeolite while the solution becomes weaker in this ion. The experimental values of K are about 1.02, or of the same order as K for isotopic exchange with mass differences of the order of 10-15% in chemical reactions at low temperatures. Of the two examples, the adsorption of neon isotopes is simpler, since the adsorbate is a gas, and its desorption corresponds to simple evaporation or dissociation.

The adsorptional separation of gases has been studied in greater detail for molecular hydrogen. The work was carried out at low temperatures on active carbon and silica gel by Harteck et al. [38]. The isotope effect was greater on silica gel than on active carbon, and decreases of pressure and temperature were shown to be advantageous [39]. The problem was studied in great detail by Mellkonian and Reps [40], who investigated the influence of the degree of covering on the coefficient of separation on silica gel. Separate determinations were made of the equilibrium constants and separation coefficients in desorption, which contained the additional kinetic factor $\sqrt{2}$, i.e., $\sqrt{\frac{m_{D_2}}{m_{H_2}}}$.

Table 16 gives the equilibrium constants for 0.0130 cc adsorbate per g, corresponding to very low degrees of covering.

TABLE 16

Equilibrium Constants for Adsorption of Hydrogen on Silica Gel at Very Low Degrees of Covering, after Mellkonian and Reps [40].

T, °K	K
20	40±10
78	4.5±0.2
90	3.0±0.2

These data satisfactorily fit the equation $K = 0.21e^{480/RT}$. According to the statistical theory, 480 cal/mole is the zero-point energy difference ΔE_0. It is close to the difference of the calorimetric heats of adsorption of D_2 and H_2 at these temperatures and to $Q_{ads.\,D_2} - Q_{ads.\,H_2}$, calculated from the adsorption isotherms. In all cases the observed values of the separation coefficient were 1.2-1.3 times the values of K $\sqrt{2}$, i.e., they included a second kinetic factor of the order of 1.2-1.3, which cannot be directly attributed to differences of mass. Consequently, the total value of the kinetic separation factor (see Chapter IV) is approximately $\sqrt{2}\cdot 1.25$, or about 1.8.

For mixtures of CH_4 with CD_4, and for neon containing Ne^{20} and Ne^{22}, the authors also found appreciable separation coefficients at low degrees of covering, but in this case ΔQ_0 was considerably less, and therefore the principal separation effect was kinetic in origin. The significance of inhomogeneity of the surface, and increased adsorption coefficients in active regions with high heats of adsorption, were additionally confirmed by ingenious experiments on "leveling" of the potential contour of the silica gel surface by blocking some of the centers with molecules of carbon dioxide.

The adsorption of gases which occurs without changes of molecular size, i.e., without association or dissociation, obeys simple laws which relate the adsorption to the masses of molecules differing in isotopic composition. Here, as in chemical exchange reactions, the determining values are the differences in the values u_i of the zero-point vibration energies. Both values refer to the adsorbent—adsorbate bond. In ion exchange adsorption the relationships are more complex, as the zero-point energies and vibrational frequencies both of ions adsorbed on the surface and of solvated ions change simultaneously. The algebraic sum of these two effects, acting in opposite directions, can lead in some cases to accumulation of the heavy isotope on the adsorbent, and in others, as observed by Taylor and Urey, of the lighter isotope.

b) Theoretical evaluation

For a rough estimate of the isotope effect in gas adsorption equilibria, a comparison of desorption with dissociation may be used. In both cases some bonds are broken, and some of the vibrational and rotational degrees of freedom are replaced by translational. As was shown earlier, in reversible dissociation the heavier isotope accumulates in the original molecules and the lighter in the dissociation products. This should also be true for adsorption treated as dissociation. Therefore the equilibrium constants for the processes

$$\begin{aligned}&\text{ads. }X + \dot{X} = \text{ads. }\dot{X} + X,\\ &\text{ads. }AX + A\dot{X} = \text{ads. }A\dot{X} + AX\end{aligned} \qquad (117)$$

should be greater than unity when $m_{\dot{X}} > m_X$, as was the case for isotopic molecules of hydrogen and neon on active carbon. In the adsorption of a mixture of $C^{12}O_2$ and $C^{14}O_2$ the content of $C^{14}O_2$ on the surface should be higher than its content in the gas. Heavy methane CD_4 should accumulate on the adsorbent from mixtures with light methane CH_4, as is found in practice [43], etc.

Differences of vibrational frequencies and of zero-point energies for the adsorptional bonds of molecules differing in isotopic composition are of primary importance for quantitative calculations. Direct determinations of these quantities are extremely difficult and have not yet been made,* but general relationships between the latter and bond energies, are adequate for approximate calculations. Their results differ little for the extreme models — a molecule vibrating relative to the solid as a whole, and a molecule (or atom) vibrating relative to one atom of the surface. In both cases the wave numbers of the vibrations should decrease with increasing mass of the adsorbed molecule, which leads to the inequality

$$K > 1; \qquad (118)$$

for the reactions represented by Equation (117), when $\dot{X} > X$

$$K = \frac{c/c_0}{c^*/c_0^*} > 1, \qquad (118a)$$

where c_0 and c_0^* are the initial concentrations of the molecules with the light and heavy isotope in the gas, and c and c^* are these concentrations after adsorption equilibrium has been established.

We now write the same expression in expanded form, using Equations (86), (98b), and (99)

$$\frac{\sigma_1}{\sigma_2}K = 1 + G(u)\,\Delta u \approx 1 + \frac{u_i\Delta u}{12} = 1 + \delta. \qquad (119)$$

The coefficient $\delta = \frac{u\Delta u}{12}$ is not large, and decreases with increase of temperature, tending to zero. There are no grounds for the inequality $\sigma_1 \neq \sigma_2$. Therefore, with increase of T, $\delta \to 0$, and the separation coefficient $f = \frac{\sigma_1}{\sigma_2} \cdot K$ tends to 1. Similar simplifications should be valid for chemisorption of gases and sorptional substitution.

---

* Some isolated attempts in this direction have been made by A.N. Terenin and his associates [41].

$$\begin{aligned}&\text{ads.} + AX \rightleftharpoons \text{ads. }X + A;\\ &\text{ads. }AX + B\dot{X} \rightleftharpoons \text{ads. }B\dot{X} + AX.\end{aligned} \qquad (117a)$$

c) Adsorption on heterogeneous surfaces

The foregoing reasoning is strictly valid only in relation to homogeneous surfaces, at which all the simultaneously adsorbed molecules are held equally firmly by the surface and vibrate at equal frequencies to an accuracy of the order of the isotope corrections. This does not exclude regular variations of Q_{ads} and ω_{ads} with degree of covering, but in such cases the isotope corrections depend on the degree of covering.

Highly heterogeneous surfaces are often met in catalysis and in adsorption on real active adsorbents [42]. The influence of this on isotope distribution can be seen most easily by comparing the adsorption equilibria of a light and a heavy isotope on homogeneous surfaces for different values of Q. Desorption equilibrium at low degrees of covering is completely analogous to dissociation equilibrium, so that it is legitimate to use Equations (86), (98b), etc.

From Equations (98b) and (119) the separation coefficient is

$$f = 1 + \sum_i G(u)\Delta u_i \approx 1 + \frac{u\Delta u}{12}. \qquad (120)$$

Let us compare the values of f_1 for the first adsorbent with high Q_{ads} and f_2 for the second adsorbent with low Q_{ads}.

We remember that in Equation (120) $u_i = hc\omega_i/kT$ and that for a harmonic oscillator consisting of two particles with different masses m_1 and m_2

$$\omega = 4.125\sqrt{\frac{p}{\mu_a}}, \qquad (121)$$

where p is the force constant. We denote the force constants and the reduced masses of adsorbed molecules of different isotopic composition on adsorbent 1 by p_1' and p_1'', and μ_1' and μ_1'' respectively.

As was stated earlier, it is practically always true that

$$p_1' = p_1'' = p_1; \qquad (122)$$

$$\Delta u_1 = \frac{hc}{kT}\omega_1' - \frac{hc}{kT}\omega_1'' = a\sqrt{p_1}\left(\frac{1}{\sqrt{\mu'_{1a}}} - \frac{1}{\sqrt{\mu''_{1a}}}\right), \qquad (123)$$

hence, from (98b)

$$f_1 = 1 + aG(u_1)\sqrt{p_1}\Delta(\mu_{1a}^{-1/2}) \qquad (124)$$

and for small values of u_1, from (120)

$$f_2 = 1 + au_1\frac{\sqrt{p_1}\Delta(\mu_{1a}^{-1/2})}{12}. \qquad (125)$$

Similarly for the second adsorbent with $Q_2 \ll Q_1$

$$f_2 = 1 + aG(u_2)\sqrt{p_2}\Delta(\mu_{2a}^{-1/2}) \qquad (124a)$$

and for small values of u_2

$$f_2 = 1 + \frac{au_2\sqrt{p_2}\Delta(\mu_{2a}^{-1/2})}{12}. \qquad (125a)$$

As an approximation, we assume, for a heterogeneous surface

$$\Delta\mu_{1a}^{-1/2} = \Delta\mu_{2a}^{-1/2}. \qquad (126)$$

The ratios of the two values of f can then be expressed as

$$f_1/f_2 = \frac{1 + a\Delta(\mu_{1a}^{-1/2})\,G(u_1)\sqrt{p_1}}{1 + a\Delta(\mu_{2a}^{-1/2})\,G(u_2)\sqrt{p_2}} \qquad (127)$$

or, for small values of u_1 and u_2, taking $\mu_{1a} \approx \mu_{2a}$,

$$f_1/f_2 = \frac{[1 + au_1\sqrt{p_1}\,\Delta(\mu_{1a}^{-1/2})]/12}{[1 + au_2\sqrt{p_2}\,\Delta(\mu_{2a}^{-1/2})]/12} \approx 1 + b\,(p_1 - p_2), \qquad (127a)$$

where $b = \frac{14.2}{\Delta\mu}\,\frac{}{a}\left(\frac{hc}{kT}\right)^2$;

For equal values of μ_a the force constant increases with the potential energy $p \sim D^{1/2}$; therefore for small values of u_i

$$p_1 \gg p_2 \text{ and } f_1/f_2 > 1;$$

at the same time it is obvious that at equal values of μ the frequencies are higher for greater values of Q, and therefore under equal external conditions the function G_1 applies to higher values of u than the function G_2. This increase is linear for small values of u, and slows down for moderate and large values of u (see Fig. 11, page 37). It is clear from the foregoing that $G(u_1)\sqrt{p_1} \gg G(u_2)\sqrt{p_2}$, and for any values of a_i the separation coefficient increases with heat of adsorption. Therefore in adsorptional equilibrium the concentration of heavy molecules should be higher on the first adsorbent than on the second. For small values of u_1 and u_2,

$$f_1/f_2 \cong 1 + b\,(Q_1^{1/2} - Q_2^{1/2}). \qquad (127b)$$

It follows from this that on a widely heterogeneous surface at a given temperature the isotopic corrections for regions with different Q should assume all values from a certain maximum value corresponding to Q_{max} to a minimum value corresponding to Q_{min}. It follows also that the distribution of light and heavy molecules over the surface would be nonuniform, and this could lead to differences in the isotopic composition of molecules desorbed from the more "active" and less active regions.

Somewhat similar effects should be observed also in adsorption on uniform surfaces with heats of adsorption which vary as the result of interaction between the molecules, whatever the nature of this interaction. The difference is that if the surface inhomogeneity is "biographical" only a part of the molecules adsorbed on the surface between θ_i and $\theta_i + \Delta\theta_i$ has heat of adsorption Q_i. All the previously adsorbed molecules retain their former Q and the former separation coefficient. With variable Q_i as the result of interaction of all the adsorbed molecules at a given θ, the values of Q are the same, and therefore not only is $\Delta\theta_i$ adsorbed with new values of f_i and K, but the values of f_i and K also change for all the previously adsorbed molecules, creating the possibility for additional exchange. This may serve as a basis for distinction between a "biographically" heterogeneous surface and a surface with induced heterogeneity or repulsion. With Q_i decreasing as the result of interaction in the layer with increasing covering, the situation will be only qualitatively the same as in equilibrium adsorption on widely heterogeneous surfaces, starting with regions with maximum Q_i. However, this is not the only possible type of relationship

In the terminology we have adopted for the theory of adsorption on heterogeneous surfaces, the adsorption potential for molecules differing in isotopic composition always varies symbatically, and molecules of greater mass exhibit the same behavior as, according to our theory, molecules of higher polarizabilities [42]. In the use of this analogy it is necessary to remember its formal nature and the fact that the differences between the adsorption constants of isotopic molecules are very small. For this last reason the separation of isotopes in the different regions is always only partial, and f can become large only at very low temperatures.

The above characteristics of equilibria at widely heterogeneous surfaces are important in the evaluation of the possible complications caused by isotope corrections in the use of the differential isotopic method [43]. In their turn, these isotopic corrections conceal the possibility (as yet unutilized) for detection and study of the relationship between heats of adsorption and the degree of covering during desorption, and also for elucidation of the origin of this relationship.

By means of the above theory of isotopic corrections in adsorption it is possible to estimate the magnitude

of the corrections in adsorptional separation of substances and in adsorption analysis of the products of complex reactions.

§13. Isotope Effects in Evaporation and Distillation

In the use of tagged atoms in kinetic studies it is often necessary to perform radiometric determinations on distillation fractions. An example is the separation of the ethane–ethylene fraction from methane and the propane–propylene fraction in studies of the distribution of C^{14} between the products of pyrolysis and cracking of hydrocarbons, carried out with the participation of molecules tagged with C^{14}, such as tagged butylene or tagged ethane.

Determination of radioactivity distribution is at the same time an excellent method for verifying the completeness of separation during distillation and for choosing the optimum conditions for the latter. In this connection it is desirable to estimate the possible vapor pressure differences between molecules of different isotopic composition. This question has been studied both theoretically and experimentally in relation to the application of fractional distillation to isotope separation [24].

The theory of isotope effects in evaporation has the same basis as the theory of isotope effects in desorption, which is a peculiar form of evaporation of adsorbed molecules. The application of statistical methods in this case yields isotopic corrections of the same order of magnitude as for chemical equilibria. In particular, in this case, as in desorption, the volatility of light molecules is higher than that of heavy molecules.

We will give a few examples of the saturated vapor pressure ratios $\pi = p_1/p_2$ for compounds differing in isotopic composition. For example, for light and heavy nitrogen (N_2^{14} and N_2^{15}) at $T = 73$°K $\pi = 1.009$

Table 17 gives the values of π for two forms of ammonia, with heavy and light nitrogen.

TABLE 17

Ratio of Saturated Vapor Pressures of Isotopic Ammonia Molecules $N^{14}H_3/N^{15}H_3$ [24]

T, °K	$\pi = p_1/p_2$
200	1.0051
225	1.0033
250	1.0019

The table shows that in separation by distillation, as in any other separation effects based on chemical processes and changes of state of aggregation, π falls rapidly with increase of temperature. The same is also found for water of different isotopic composition, H_2O^{16} and H_2O^{18}.

The variation of π with temperature is exponential. According to Kirshenbaum, the experimental data satisfy the expression $\log \pi = \frac{3.20}{T} - 0.00680$. For a given temperature the ratio of $\delta = \pi - 1$ for water H_2O^{16} to that for water H_2O^{17} is about a half of the corresponding ratio for H_2O^{18}.

TABLE 18

Saturated Vapor Pressure Ratio for H_2O^{16}/H_2O^{18} [24]

T, °K	$\pi = p_1/p_2$	T, °K	$\pi = p_1/p_2$
300	1.0110	375	1.0051
325	1.0085		
350	1.0067	400	1.0036

For the lightest carbon compounds, such as CH_4, CO, or CH_2O, the values of π obtained on replacement of C^{12} by C^{14} or C^{13} are close to those given in Tables 17 and 18. For more complex molecules, such as benzene or diphenylamine, the vapor pressure changes which result from replacement of atoms of the commonest isotope C^{12} by C^{13} and C^{14} are considerably less.

It is seen that all the observed values of π are small and do not greatly exceed the accuracy limits of the usual determinations of tagged atom contents. Therefore, unless the effect becomes cumulative owing to frequent repetition of the process or to utilization of small residues from the distillation of very large masses, isotopic corrections in evaporation may in practice be neglected for compounds of all elements except hydrogen. Table 19 illustrates the vapor pressure differences which result from replacement of H by D.

TABLE 19

Vapor Pressures of Liquid Heavy Water [44]

T, °C	Vapor pressure of D_2O mm, Hg	Vapor pressure of D_2O, atm.	$\pi = p_{H_2O}/p_{D_2O}$	T, °C	Vapor pressure of D_2O mm, Hg	Vapor pressure of D_2O, atm.	$\pi = p_{H_2O}/p_{D_2O}$
3.82	5.05	0.00664		110	1028	1.353	1.045
10.0	7.79	0.01025	1.18_2	120	1434.5	1.888	1.038
20.0	15.2	0.0200	1.15_4	130	1963.5	2.584	1.032
30.0	28.0	0.0368	1.13_7	140	2640	3.474	1.027
40.0	49.3	0.0647	1.12_2	150	3493	4.596	1.022
50.0	83.6	0.1100	1.107	160	4554.5	5.993	1.018
60.0	136.6	0.1797	1.094	170	5857	7.707	1.014
70.0	216.1	0.2843	1.081	180	7438.5	9.788	1.011
80.0	331.6	0.4363	1.071	190	9337.5	12.29	1.008
90.0	495.5	0.6520	1.061	200	11597	15.26	1.005
100.0	722.2	0.9503	1.052	210	14261	18.77	1.003
101.431	760.0	1.000		220	17379	22.87	1.001
				230	21001	27.63	0.998_0
				240	25207	33.17	0.995_8
				371.5		218.6	

Statistical analysis shows that the vapor pressure of HDO should be the geometric mean of the vapor pressures of H_2O and D_2O. It is therefore possible to use Table 19 for calculation of π for H_2O relative to HDO for any of the temperatures in the table. For this, $\delta_{D_2O} = \pi - 1$ should be divided by 2, and the value of $\delta_{HDO} = \frac{\delta_{D_2O}}{2}$ obtained is then used to find $\pi_{HDO} = 1 + \delta_{HDO}$. The relationship $\delta_{HDO} = 0.5\,\delta_{D_2O}$, which follows from the theory, is confirmed experimentally. High values of π for H_2O/HDO and H_2O/D_2O correspond to considerable differences of the heats of evaporation; and since p_{D_2O} is less than p_{H_2O}, the heats of evaporation at constant pressure ΔH_{D_2O} are higher than ΔH_{H_2O}. For 25°C, very careful measurements performed by many authors give the ratio $\Delta H_{D_2O}/\Delta H_{H_2O} = 1.03145$. Since $\Delta H^{25°}_{H_2O} = 10515$ cal/mole, this ratio corresponds to $\Delta H^{25°}_{D_2O} = 10846$. The difference between these two values is 331 cal/mole. Data for other temperatures are given in Table 4 of the Appendix. For H_2O^{18}/H_2O^{16} the difference of the heats of evaporation, determined with much less accuracy, is about 15 times as small (20 cal.).

The above analysis of isotope effects in desorption and evaporation is based on the analogy with chemical substitution and dissociation processes. A more rigid examination may be carried out if mixtures of molecules of different isotopic composition in any state of aggregation are regarded as solutions of substances of unlimited miscibility, the interactions of which follow identical laws. In classical statistical mechanics the difference of chemical potentials of two mixing species 1 and 2 [45] is

$$\mu_{01} - \mu_{02} = \frac{3}{2} kT \ln \frac{m_1}{m_2}, \qquad (128)$$

where m_1 and m_2 are the masses of two molecules differing in isotopic composition only. This difference, which represents the difference of the chemical constants of the two molecules multiplied by kT, is the same for all phases of a given substance. At equilibrium the chemical potentials of any component should be equal in all phases [46]. Since the differences $\mu_{01} - \mu_{02}$ are equal for different phases, the phase equilibrium equation should be the same for the molecules being compared, and therefore the saturated vapor pressures of all isotopes, taken as pure individual substances, are equal. This is also true for vapor pressures of any molecules differing in isotopic composition only, such as $C^{12}H_4$, $C^{14}D_4$, $C^{13}HDT_2$, etc. Differences of volatility and adsorbability, as in the case of the chemical equilibrium constants, can only arise in consequence of the quantization of energy and the operation of the laws of quantum mechanics in microsystems.

Because of the almost complete identity of interaction, all isotopic mixtures obey the ideal solution laws, and, in particular, Raoult's law, according to which the partial pressure of each over a liquid or solid mixture is equal to the product of the pressures of the forms taken in pure isotopic form, p_{01} and p_{02}, multiplied by the mole fractions γ of these forms (molecules, atoms) in the solution

$$\gamma_1 = \frac{N_1}{N} \text{ and } \gamma_2 = \frac{N_2}{N}, \qquad (129)$$

where N_1 is the total number of molecules of one isotopic composition, N_2 is the total number of molecules of the second isotopic composition, and $N = N_1 + N_2$. For the above it follows that

$$\begin{aligned} p_1 &= \gamma_1 \cdot p_{01} \\ p_2 &= \gamma_2 \cdot p_{02}. \end{aligned} \qquad (129a)$$

To calculate the vapor pressures of pure isotopic forms, such as $C^{12}H_4$ or $C^{14}D_4$, etc., it is necessary to know the total statistical sums of their molecules in the condensed phase and in the gas. In the simplest case of a condensed phase consisting of atoms, the chemical potential is given by the equations

$$\mu = \mu_{\text{class}} + \frac{h^2}{24mkT} \cdot \overline{F^2}, \qquad (130)$$

where

$$\overline{F^2} = \left(\frac{\partial \overline{U}}{\partial x}\right)^2 + \left(\frac{\partial \overline{U}}{\partial y}\right)^2 + \left(\frac{\partial \overline{U}}{\partial z}\right)^2 \qquad (131)$$

is the mean square of the force exerted on one atom in a condensed system by all the others.* In calculations of the chemical potential of a monoatomic vapor the latter is considered as consisting of particles which obey the laws of classical mechanics, as because of the smallness of the translational quanta, the translational energy spectrum is continuous. The conditions $\mu_{\text{cond}} = \mu_{\text{vap}}$, obligatory for each of the isotopes separately, makes it possible to calculate the quantum correction for the classical value of the saturated vapor pressure, and for the difference of two pressures it gives the expression

$$\Delta p_{\text{isot}} = p_{01} - p_{02} = p_0 \frac{h^2 \overline{F^2}}{24 (kT)^2} \left(\frac{1}{m_1} - \frac{1}{m_2}\right); \qquad (132)$$

where p_0 is the classical value of the equilibrium vapor pressure, the same for both isotopic atoms, while the fraction with p_0 is obtained from the quantum correction in Equation (130). To calculate Δp_{isot} it is necessary to calculate the values of $\overline{F^2}$ for different temperatures or to know the dependence of $\overline{F^2}$ on the temperature. Conversely, having determined Δp_{isot} for known m_1 and m_2, we can calculate $\overline{F^2}$.

The vapor pressure equations for pure forms of complex molecules of different isotopic composition should be similar, as the most characteristic intramolecular vibrations should not vary appreciably in evaporation. We may note here that the expression (132) may form the basis of sorption equilibrium analysis.

§14. Chemical Equilibria in Non-Ideal Heterogeneous Systems

The statistical theory equations of isotope equilibria have been derived on the basis of far-reaching simplifying assumptions, and the final formulas derived in the foregoing sections are applicable without qualification only to gases or liquids if intermolecular forces are small. However, in the temperature region in which isotopic corrections are significant, homogeneous liquid-phase reactions and heterogeneous reactions often involving solids predominate. Fortunately, experience shows that the practical applicability of these equations is not confined to homogeneous gaseous systems close to ideality. This indicates the existence of unconsidered factors which appreciably extend the range of applicability of the theory. It is easy to demonstrate that these calculation methods can be legitimately extended to isotopic exchange in real gases, even very far removed

---

*U is the potential energy. Its partial derivatives with respect to the coordinates x, y, and z represent the forces which retain the particle in the lattice.

from ideality. For such gases the form of the thermodynamic relationships characteristic for ideal gases may be retained if the true partial pressures are replaced by fugacities which, like concentrations, may be written as the products of the corresponding values for the ideal gases in the mixtures and the activity coefficients; $f_i = p_i \cdot a_i$. The equilibrium constant then resolves into two fractions of similar form, of which one contains only partial pressures, and the other, only activity coefficients.

It is natural to assume that the frequencies of internal vibrations and the corresponding statistical sums will remain unchanged for gaseous molecules taking part in the exchange. The influence of the isotopic composition of the molecules on the energy of intermolecular interaction is negligibly small, and therefore the fraction containing $a_i^{\nu_i}$ may be taken as equal to unity, and the equilibrium constant for ideal gases may be used in the calculations.

In the liquefaction of gases the system of vibrational frequencies in many cases remains unchanged, and their numerical values ω_i do not change by more than 5%. Thus, for example, in the case of sulfur dioxide the fundamental frequencies 1151.2; 519; and 1361 cm^{-1} have been found for the gas, and 1144.3; 524; and 1336.0 respectively for the liquid. A similar situation is often found for solutions. Only in the case of substances with a tendency to association do some of the characteristic vibrational frequencies disappear and become replaced by others. In particular, this is typical of many hydroxylic compounds (alcohols, organic acids, etc.) with a tendency to association with hydrogen bond formation. In cases when the fundamental vibrational frequencies of the molecules remain almost unchanged, it is natural to expect that the equations derived for ideal gases will be applicable to isotopic exchange equilibria between molecules in the liquid phase and also between gas and liquid molecules. In the process of solution, accompanied by far-reaching chemical changes of all or most of the dissolved molecules, there are no grounds for expecting such agreement; but even in such cases satisfactory agreement may be expected with the use of experimentally determined characteristic vibrational frequencies of the dissolved molecules.

This result is the consequence of considerable differences between the stability of intramolecular and intermolecular forces. The situation is different in changes of the state of aggregation, such as evaporation, when the intermolecular forces are predominant. In such cases anomalous isotopic effects are also possible. Typical examples are cited in the tables of the first section of the Appendix, taken from the recently published paper by I.B. Rabinovich, N.N. Sokolov and P.I. Artyukhin [46].

The foregoing theory is applicable without substantial modification to isotopic exchange equilibria involving solids only if the crystal lattices are of a molecular character, when intramolecular vibrational frequencies characteristic for gases and vapors are retained. Thus, in particular, it is easy to find for crystalline benzene at −80° the fundamental frequencies 3089 and 3034, analogous to the frequencies 3099 and 3045 found for the vapor and 3090 and 3035 for the liquid. Therefore hydrogen-exchange equilibria between benzene vapor and crystals can be calculated, although only very roughly, with the aid of statistical sums for ideal gases. The theory is inapplicable to isotopic exchange involving atomic, ionic, or metallic lattices.

According to Debye's universally accepted theory, thermal vibrations belonging to the crystal as a whole are propagated in a crystal lattice with sonic velocities. Their frequencies, which cannot be referred to individual atoms, completely fill the range from $\nu = 0$ to $\nu = \infty$. The distribution of different frequencies in the continuum is characterized by the distribution function $\rho(\nu)$. Its exact form is complex. Debye used $\rho(\nu) = \frac{g\nu^3}{\nu_{max}^3}$ at

$$\nu \leqq \nu_{max} = \nu_D \text{ and } \rho(\nu) = 0 \text{ at } \nu \geqq \nu_D .$$

On the assumptions made, the logarithm of the statistical sum is given by the expression

$$\ln Z(T) = -\frac{12\pi V}{C^3}\int_0^{\nu_D}\nu^2 \ln\left(1 - e^{-h\nu/kT}\right)d\nu = -3N\ln\left(1 - e^{-\theta_D/T}\right) + 3N\frac{T^3}{\theta_D^3}\int_0^{\theta_D/T}\frac{u^2}{e^u - 1}du, \quad (133)$$

where C is the velocity of sound, $\theta_D = h\nu_D/k$, and the second term of the last expression is the Debye function $D(\theta_D/T)$, widely used in thermodynamic calculations [47].

The above expressions for $\ln Z$ characterize the atomic lattice. For a crystal composed of n-atomic molecules, the statistical sum may be approximately represented by the product of the statistical sum for a crystal lattice in which 3N normal vibrations are distributed by frequencies in accordance with the Debye theory, and the unchanged internal statistical sum for the molecules. In the development of an extended statistical theory of isotope exchange involving solids, it is necessary to take into consideration the characteristic features of the vibrational energy of the crystal, and to use the frequency continuum. This was first done by I.M. Lifshits and G.I. Stepanova.*

It is usual to regard equilibrium mixtures of isotopic molecules in any state of aggregation as ideal solutions. Lifshits and Stepanova showed that this generally accepted view is not valid for solid solutions. The propagation velocity of sound waves C depends on the density of the medium, and it should therefore change when atoms in a lattice are replaced by their isotopes. Since C is related to ν_D, the vibrational spectrum should change also. The authors derived exact formulas for the dependence of the spectrum and the free energy of lattice vibration on the isotopic composition, and have given approximate simple relationships for long-wave vibrations, insensitive to lattice structure, which play the main role in the low temperature region.

If dispersion is ignored, the vibrational part of the free energy of a solid isotopic solution coincides with the vibrational part of the free energy of the isotope if the mass of the latter is replaced by the average mass of the atoms $\overline{m} = m_1(1-\gamma) + m_2\gamma$, where m_1 and m_2 are the masses of the two isotopes and γ is the concentration of the second isotope in the solid phase, expressed as a mole fraction. The thermodynamic potential Φ of the solution is then given by the expression

$$\Phi = N\mu(\overline{m}) + NkT\{\gamma\ln\gamma + (1-\gamma)\ln(1-\gamma)\}; \quad (134)$$

where $\mu(\overline{m})$ is the Gibbs chemical potential of the solution as a function of the average mass of its atoms. From this equation the authors derive the following expressions for the equilibrium vapor pressure over a solid solution of isotopes and for the ratio of the mole fractions in the vapor and solid phases:

$$p = (1-\gamma)p_1 + \gamma p_2 - \frac{1}{2}p_{1,2}\Delta m^2(1-\gamma)\gamma\mu''/kT$$

and

$$\gamma_{gas} - \gamma = \gamma(1-\gamma)\left\{\frac{p_2 - p_1}{p} - \frac{(1-\gamma)\gamma\Delta m^2\mu''}{2kT}\right\}, \quad (135)$$

which differ from the equations for ideal solid solutions by the terms in Δm^2 and μ''. In Equations (135) p_1 and p_2 are equilibrium vapor pressures of crystals containing the 1st or 2nd isotope only. In the correction terms, μ'' is the second derivative of the chemical potential. Deviations from ideality increase with decrease of T. When $\Delta m^2\mu''/kT$ ceases to be small, to construct the equilibrium diagram it becomes necessary to use the exact expressions

$$p_1 = (1-\gamma)p_1 \cdot \exp\left(-\frac{\gamma^2\Delta m^2}{2}\cdot\mu''/kT\right) + \gamma p_2 \cdot \exp\left(-\frac{(1-\gamma)^2\cdot\Delta m^2}{2}\cdot\mu''/kT\right)$$

and

$$(\gamma_{gas} - \gamma) = \gamma(1-\gamma)\frac{1}{p}\left\{p_1 \cdot \exp\left(-\frac{C^2\Delta m^2}{2}\cdot\mu''/kT\right) + p_2 \cdot \exp\left(-\frac{(1-\gamma)^2\Delta m^2}{2}\mu''/kT\right)\right\}. \quad (136)$$

Equations (135) and (136) correspond to the classical Konovalov phase diagram without maxima or minima.

Having augmented the statistical theory of isotope exchange for ideal gases by the evaporation theory of Lifshitz and Stepanova, we are able to calculate equilibria involving gases and solids. The theory has not, as yet, been verified by experimental data. This is true also for the theory of isotopic equilibria in solid phases, developed by the same authors.

§ 15. Relationship Between Enrichment Factors and Equilibrium Constants

To sum up the foregoing, we reach the conclusion that in the main types of processes met in kinetics and catalysis, thermodynamic isotope effects are slight for all elements except hydrogen. In most cases they may be ignored in the use of isotopes as tagged atoms. Less frequently it may be advisable to introduce small corrections into the observed changes of isotope distribution between atoms, molecules, and bonds. The magnitude of these corrections is easily calculated. The position is essentially different in work on isotope sepa-

---

*By courtesy of the authors I have been able to use the results of their valuable work (first reported at the Ukrainian Physicochemical Conference in Kiev in 1954).

ration, where effective methods of extensive enrichment and even complete separation are often based on these slight differences. In such work even very small differences in the magnitude of the separation functions and isotope corrections for the equilibrium constants are very significant as they have a strong influence on the efficiency of the equipment used. Without a detailed discussion of this question, which may be found in many publications [24], we will only cite two equations which connect the enrichment factor α with the equilibrium constant (138), and the enrichment attainable for a given value of α with the number of individual operations (137). In Equation (137), s is the number of theoretical plates in distillation, the number of consecutive adsorption operations in chromatographic separation, etc.

With s plates, in the simplest case of a low absolute concentration of one of the isotopes, the enrichment is

$$\alpha(s) = \alpha^s. \tag{137}$$

At the same time, to a good degree of approximation,

$$\alpha = \left(\frac{K_1}{K_2}\right)^{\frac{1}{mn}}, \tag{138}$$

where m and n are the numbers of atoms of element X in the molecules involved in the exchange; for example, m = 2 and n = 3 in exchange between SH_2 and ND_3.

Our tables in most instances refer to equations with m and n = 1, and therefore

$$\alpha = \frac{K_1}{K_2} \tag{138a}$$

§ 16 Isotope Effects in Hydrogen Equilibria

a) The simplest reactions of hydrogen

In studies of chemical reaction mechanism with the aid of tagged atoms, hydrogen isotopes are outstanding both in the number of published papers and in the importance of the results obtained. For no other element are there such abundant data on the influence of isotopic composition on the structure of molecules and solids, on their energetics and on their reactivity. Hydrogen-ion transitions play an outstanding role in the kinetics of reactions in solution. In practical catalysis, hydrogenation and dehydrogenation comprise one of the most extensive and important groups of catalytic reactions, some of which are carried out at low temperatures, which are favorable for isotope effects. The magnitude of the latter is much greater than for reactions of other elements. The isotope corrections are especially large for processes involving only molecular hydrogen in different isotopic forms. These include

1. Reactions of isotope exchange between hydrogen molecules:

$$\left.\begin{aligned}
&\text{a)}\quad H_2 + D_2 \rightleftarrows 2HD && K_a = \frac{[HD]^2}{[H_2][D_2]}\\
&\text{b)}\quad D_2 + T_2 \rightleftarrows 2DT && K_b = \frac{[DT]^2}{[D_2][T_2]}\\
&\text{c)}\quad H_2 + T_2 \rightleftarrows 2HT && K_c = \frac{[HT]^2}{[H_2][T_2]}\\
&\text{d)}\quad H_2 + DT \rightleftarrows HT + DH && K_d = \frac{[HT][DH]}{[H_2][DT]}\\
&\text{e)}\quad D_2 + HT \rightleftarrows DH + TD && K_e = \frac{[DH][TD]}{[D_2][HT]}\\
&\text{f)}\quad T_2 + HD \rightleftarrows HT + DT && K_f = \frac{[HT][DT]}{[T_2][HD]}
\end{aligned}\right\} \tag{139}$$

2. Conversion of molecules of para-hydrogen p-H_2, into molecules of ortho-hydrogen, o-H_2:

$$\left.\begin{aligned}
&\text{a)}\quad p\text{-}H_2 \rightleftarrows o\text{-}H_2 && K_a = \frac{[o\text{-}H_2]}{[p\text{-}H_2]};\\
&\text{b)}\quad p\text{-}D_2 \rightleftarrows o\text{-}D_2 && K_b = \frac{[o\text{-}D_2]}{[p\text{-}D_2]};\\
&\text{c)}\quad p\text{-}T_2 \rightleftarrows o\text{-}T_2 && K_c = \frac{[o\text{-}T_2]}{[p\text{-}T_2]}
\end{aligned}\right\} \tag{140}$$

3. Exchange between molecules and atoms:

$$\left.\begin{aligned}
&\text{a)}\quad D_2 + H \rightleftarrows DH + D && K_a = \frac{[DH][D]}{[D_2][H]};\\
&\text{b)}\quad T_2 + H \rightleftarrows TH + T && K_b = \frac{[TH][T]}{[T_2][H]};\\
&\text{c)}\quad H_2 + D \rightleftarrows DH + H && K_c = \frac{[DH][H]}{[H_2][D]};\\
&\text{d)}\quad T_2 + D \rightleftarrows TD + T && K_d = \frac{[TD][T]}{[T_2][D]};\\
&\text{e)}\quad H_2 + T \rightleftarrows HT + H && K_e = \frac{[HT][H]}{[H_2][T]};\\
&\text{f)}\quad D_2 + T \rightleftarrows DT + D && K_f = \frac{[DT][D]}{[D_2][T]}
\end{aligned}\right\} \tag{141}$$

4. Ortho → para transitions by a substitution mechanism with artificially introduced hydrogen atoms, which may be regarded as special cases of reactions of the preceding third type:

$$\left.\begin{aligned}
&\text{a)}\quad p\text{-}H_2 + H \rightleftarrows o\text{-}H_2 + H && K_a = \frac{[o\text{-}H_2][H]}{[n\text{-}H_2][H]};\\
&\text{b)}\quad p\text{-}D_2 + D \rightleftarrows o\text{-}D_2 + D && K_b = \frac{[o\text{-}D_2][D]}{[n\text{-}D_2][D]};\\
&\text{c)}\quad p\text{-}T_2 + T \rightleftarrows o\text{-}T_2 + T && K_c = \frac{[o\text{-}T_2][T]}{[n\text{-}T_2][T]}
\end{aligned}\right\} \tag{142}$$

5. Physical sorption and desorption of hydrogen:

$$\begin{aligned}
&\text{adsorbent} + H_2 = \text{adsorbent}\,(H_2)_{ads};\\
&\text{adsorbent} + D_2 = \text{adsorbent}\,(D_2)_{ads};\\
&\text{adsorbent} + HD = \text{adsorbent}\,(HD)_{ads}\\
&\text{etc.}
\end{aligned} \tag{143}$$

6. Chemical adsorption of hydrogen:

$$\begin{aligned}
&\text{a)}\quad H_2 + \text{adsorbent} = \text{adsorbent}\,(H_{ads})_2;\\
&\text{b)}\quad D_2 + \text{adsorbent} = \text{adsorbent}\,(D_{ads})_2;\\
&\text{c)}\quad HD + \text{adsorbent} = \text{adsorbent}\,(H_{ads})(D_{ads}).
\end{aligned} \tag{144}$$

7. Dissociation and recombination of hydrogen:

$$\left.\begin{aligned}
&H_2 \rightleftarrows 2H;\\
&D_2 \rightleftarrows 2D;\\
&HD \rightleftarrows H + D;\\
&HT \rightleftarrows H + T\\
&\text{etc.}
\end{aligned}\right\} \tag{145}$$

8. Neutralization and formation of hydrogen ions:

a) Neutralization of H^+, D^+, and T^+.

$$\left.\begin{aligned} H^+ &\overset{e}{\rightleftarrows} H; \\ D^+ &\overset{e}{\rightleftarrows} D; \\ T^+ &\overset{e}{\rightleftarrows} T. \end{aligned}\right\} \qquad (146)$$

b) Formation of H^-, D^-, and T^-

$$\left.\begin{aligned} H &\overset{e}{\rightleftarrows} H^-; \\ D &\overset{e}{\rightleftarrows} D^-; \\ T &\overset{e}{\rightleftarrows} T^-. \end{aligned}\right\} \qquad (147)$$

9. Ionization of hydrogen in solutions.

The above nine types of processes do not exhaust the range of hydrogen reactions of the class in question.* Reactions of the type 1-6 are much favored for kinetic investigations because of their simplicity and similarity to hydrogenation reactions. Dissociation and recombination (Type 7) are very often met in homogeneous and heterogeneous kinetics of thermal reactions of hydrogen, and its reactions in the electric discharge. Equilibrium constants for Type 1 reactions are given in Table 23, and for Type 7 in Table 3. Reactions of Types 8 and 9 play an important role in electrochemistry. The approximate equations derived in §7 for isotopic exchange of other elements cannot always be regarded as satisfactory for hydrogen at low temperatures. This makes necessary a separate examination of isotope effects for hydrogen and its compounds.

b) Molecular hydrogen

Table 20 shows the zero-point energies of isotopic forms of molecular hydrogen and of some of its compounds, used for calculations of its equilibria.

It is seen from Table 20 that, at present, absolute values of E_0 calculated from spectroscopic data are not very reliable. There are as yet no other methods for measurement of E_0.

Table 20 shows that there are great differences among the vibrational and rotational constants of different isotopic forms of molecular hydrogen, which naturally leads to appreciable differences in all the thermodynamic quantities characterizing free molecules. Considerable differences are also found for the latent heats of change of state. This is illustrated by the small Table 21, which contains data on the molar heats of fusion and vaporization of three isotopic forms of hydrogen and three isotopic forms of water. Here also the differences are fairly considerable, being 19 cal /mole for the heats of fusion and 82.6 cal /mole for the heats of vaporization of D_2 and H_2. The heat of fusion and vaporization differences between tritium and protium should be approximately 1.5 times as large. The absolute changes in the values of λ on isotopic substitution of H by D in water are still greater, being 79 cal /mole for fusion and 208 cal /mole for vaporization. Substitution of two atoms of light hydrogen by two atoms of deuterium changes λ_f by 68% and λ_v by 37%. In the case of water $\frac{\Delta\lambda}{\lambda}$ for evaporation is also appreciably less than for fusion, both ratios being more than 10 times smaller than the corresponding ratios for molecular hydrogen. Both in the case of hydrogen and in the case of water all values of λ increase with increasing molecular weight.

Three characteristics of molecular hydrogen are important in calculations of its thermodynamic functions: 1) difference between the symmetry numbers of monoisotopic and diisotopic molecules; 2) the existence of ortho- and para-forms in diatomic monoisotopic molecules, and 3) the relatively large distance between rotational levels:

---

*For example, no mention has been made of various photochemical and radiochemical reactions of hydrogen in which, in addition to free atoms and atomic ions, molecular ions and excited molecules, atoms, and ions may also be formed.

$$\Delta\nu_{rot} = 2B_0 = \frac{2h}{8\pi^2 I_0 c}. \qquad (148)$$

The first characteristic is important at all temperatures, while the second and third are largely important in the low-temperature region.

TABLE 20

Zero-Point Energies of Some Simple Isotopic Hydrogen Molecules, after Zeiss [48]

Molecule	H_2	HD	D_2	DT	T_2	HT	Notes*
E_0, cal/mole	6253 6183.5	5423 5366.4	4433 4394.5	4049 —	3625 —	5114 —	Libby's data Clusius's data
Molecule	H_2O	HOD	D_2O	DOT	T_2O	HOT	
E_0, cal/mole	13241 13097	11480 11393	9682 9527	8951 —	8148 —	10771 —	Libby's data Clusius's data
Molecule	HCl	DCl	HBr	DBr	HI	DI	
E_0, cal/mole	4214.4	3030.4	3808	2720	3245.7	2310.0	Clusius's data

*The difference between the two series of figures in the table is due to the different values of the anharmonicity constants used for calculations of E_0

TABLE 21

Effect of Replacement of Protium by Deuterium on the Latent Heats of Fusion and Vaporization of Molecular Hydrogen and Water (cal /mole)

Substance	Latent heat of fusion, λ_f	Latent heat of vaporization λ_v	$\Delta\lambda_f$	$\frac{\Delta\lambda_f}{\lambda_f}$	$\Delta\lambda_v$	$\frac{\Delta\lambda_v}{\lambda_v}$
		Hydrogen				
H_2	28.0	219.7	+19.0	+68%	+82.6	+37%
D_2	47.0	302.3	—10 0	—21.2%	—39.3	—13%
HD	37.0	263				
		Water				
H_2O	1436	9719	+79 0	+5 5%	+208	+2.1%
D_2O	1515	9927				

Right up to room temperatures $h\nu_{rot} > kT$ and therefore, at low temperatures, rotational statistical sums cannot be replaced by integrals. Even in the liquid air temperature region the error which such replacement introduces is so large that the replacement becomes meaningless, while hydrogen is often used at its boiling point. In calculations of statistical sums for diisotopic molecules of hydrogen there are no para- and ortho-forms to be considered, and it is sufficient to summate the terms $ge^{-E_{rot}/kT}$ for only one molecular type.

In particular, the expression for HD may be written as

$$\sum_{\text{rot}} \text{HD} = \sum 6(2J+1)e^{J(J+1)\frac{B}{kT}} \qquad (149)$$

where J can have any values from 0 to ∞.

For monoisotopic molecules the rotational statistical sum is composed of the statistical sums for the para- and ortho-forms. For the first of these sums in the case of light hydrogen the values of the rotational quantum numbers J are even, and g = 1; for the ortho-form the rotational quantum numbers are odd, and g = 3.

Hence we have Equation (150)

$$\left.\begin{aligned}\sum_{\text{rot}} \text{p-H}_2 &= \sum_{\substack{J\\ \text{even}}} (2J+1)e^{-J(J+1)B/kT} = 1 + 5e^{-6B/kT} + 9e^{-20B/kT} + \cdots\\ \sum_{\text{rot}} o\text{-H}_2 &= \sum_{\substack{J\\ \text{odd}}} 3(2J+1)e^{-J(J+1)B/kT} = 3(3e^{-2B/kT} + 7e^{-12B/kT} + \cdots\end{aligned}\right\} \qquad (150)$$

In deuterium the para-form is characterized by even rotational quantum numbers, and the ortho-form by odd [12]. The statistical weight, calculated from the nuclear spins, is three for para-deuterium and six for ortho-deuterium. Therefore the corresponding statistical sums have the following form:

$$\left.\begin{aligned}\sum_{\text{rot}} \text{p-D}_2 &= \sum_{\text{odd}} 3(2J+1)e^{-J(J+1)B/kT} =\\ &= 9e^{-2B/kT} + 21e^{-12B/kT} + 33e^{-30B/kT} + \cdots\\ \sum_{\text{rot}} o\text{-D}_2 &= \sum_{\text{even}} 6(2J+1)e^{-J(J+1)B/kT} =\\ &= 6 + 30e^{-6B/kT} + 54e^{-20B/kT} + \cdots\end{aligned}\right\} \qquad (151)$$

The nuclear spin of tritium is the same as that of protium, and therefore the ortho- and para-forms have the same odd and even quantum number and statistical weight characteristics. Naturally, the rotational statistical sums for p-T_2 and o-T_2 differ from the statistical sums of Equation (151) only by a considerably smaller value of B

$$B_{H_2} : B_{D_2} : B_{T_2} = 3:2:1 \qquad (151a)$$

For any temperature the constant for the ortho–para equilibrium is equal to the ratio of the rotational sums $\Sigma_{\text{ortho}}/\Sigma_{\text{para}}$. Hence

$$K_{\text{p}\to o\text{-H}_2} = K_{\text{p}\to o\text{-T}_2} = \frac{[o\ \text{H}_2]}{[\text{p-H}_2]} = \frac{3(3e^{-2B/kT} + 7e^{-12B/kT} + 11e^{-30B/kT} + \cdots)}{1 + 5e^{-6B/kT} + 9e^{-20B/kT} + 13e^{-42B/kT} +} \qquad (152)$$

and

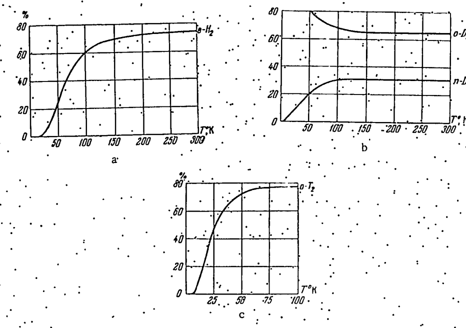
$$K_{\text{p}\to o\text{-D}_2} = \frac{[o\text{-D}_2]}{[\text{p-D}_2]} = \frac{6 + 30e^{-6B/kT} + 54e^{-20B/kT} + \cdots}{9e^{-2B/kT} + 21e^{-12B/kT} + 33e^{-30B/kT}} \qquad (152a)$$

At sufficiently high temperatures the sums may be replaced by integrals [12].

The integrals for the para- and ortho-forms differ only by the statistical weights of the even and odd levels. Therefore, at sufficiently high temperatures the equilibrium constant for light hydrogen should be equal to the ratio g_o/g_p, i.e., three for protium and tritium. For the two forms of deuterium g is 6 and 3 respectively; and therefore the equilibrium constant should be two. At sufficiently low temperatures all the molecules have the lowest of all possible rotational numbers J = 0. In light hydrogen and tritium the para-forms are characterized by even rotational quantum numbers, and therefore only this form should remain in equilibrium on sufficiently great decrease of temperature. In deuterium, on the contrary, the ortho-form is even, and it alone is retained at low temperatures. Consequently, for protium and tritium the equilibrium constant for the ortho- and para-forms changes from 0 to 3 with increase of temperature, while for deuterium it changes from infinity to 2 (Fig. 12). For calculations of the statistical rotational sums for intermediate temperatures it is necessary to know the fraction β of the ortho- and para-forms at equilibrium, to multiply the corresponding statistical sums by β_{ortho} and β_{para}, and to add the products.

$$\left.\begin{aligned}\sum_{\text{rot}} \text{H}_2 &= \beta^{\text{H}}_{\text{ortho}} \quad o\text{-H}_2 + \beta^{\text{H}}_{\text{para}} \sum_{\text{rot}} \text{p-H}_2,\\ &\text{and, for D}_2 \text{ and T}_2 \text{ respectively}\\ \sum_{\text{rot}} \text{D}_2 &= \beta^{\text{D}}_{\text{ortho}} \sum o\text{-D}_2 + \beta^{\text{D}}_{\text{para}} \sum_{\text{rot}} \text{p-D}_2,\\ \sum_{\text{rot}} \text{T}_2 &= \beta^{\text{T}}_{\text{ortho}} \sum o\text{-T}_2 + \beta^{\text{T}}_{\text{para}} \sum_{\text{rot}} \text{p-T}_2.\end{aligned}\right\} \qquad (153)$$

Therefore, for calculations of rotational sums and isotope corrections for hydrogen equilibria at low temperatures, it is necessary to know the equilibrium content of each of the molecular forms at the temperature in question. Table 22 gives the data for protium, deuterium, and tritium, calculated from the statistical sums



a

b

c

Fig. 12. Variation of equilibrium contents with temperature. a) o-H_2; b) o-D_2, c) o-T_2 [12]

Special corrections for the discrete nature of rotational levels are necessary only for different forms of molecular hydrogen. Even for such simple hydrides as HBr and HCl such corrections are usually superfluous.

Table 23 gives the theoretical values of the equilibrium constants for six isotopic-exchange reactions of hydrogen

1) $H_2 + T_2 \rightleftharpoons 2HT$
2) $D_2 + T_2 = 2DT$
3) $T_2 + HD \rightleftharpoons HT + DT$
4) $H_2 + DT \rightleftharpoons HD + HT$
5) $D_2 + HT \rightleftharpoons HD + DT$
6) $H_2 + D_2 \rightleftharpoons 2HD$

---

*With different values of B for protium and tritium, in accordance with Equation (151a).

TABLE 22

Equilibria of Ortho- and Para-Forms of Hydrogen, after Zeise [48]

T, °K	$p\text{-}H_2 \rightarrow o\text{-}H_2$ $K = \frac{p_{ortho}}{p_{para}} = \frac{x}{1-x}$ x = fraction of $o\text{-}H_2$		$o\text{-}D_2 \rightarrow p\text{-}D_2$ $K = \frac{p_{para}}{p_{ortho}} = \frac{x}{1-x}$ x = fraction of $p\text{-}D_2$		$p\text{-}T_2 \rightarrow o\text{-}T_2$ $K = \frac{p_{ortho}}{p_{para}} = \frac{x}{1-x}$ x = fraction of $o\text{-}T_2$	
	x	K	x	K	x	K
300	0.74928	2.9885	0.33333	0.50000	0.75000	3.0000
250	0.74734	2.9581	0.33331	0.49996	0.75000	3.0000
200	0.74026	2.8501	0.33327	0.49986	0.75000	3.0000
150	0.71397	2.4962	0.33246	0.49803	0.74992	2.9987
120	0.67041	2.0340	0.32916	0.49067	—	—
100	0.61380	1.5894	0.32164	0.47414	0.74925	2.9881
90	0.57118	1.3320	0.31395	0.45762	—	—
80	0.51463	1.0603	0.30141	0.43145	—	—
75	0.47908	0.9197	—	—	0.74462	2.9157
70	0.44009	0.7860	0.28162	0.39201	—	—
60	0.34431	0.5251	0.25131	0.33567	0.73263	2.7402
50	0.22946	0.29785	0.20718	0.26132	0.71211	2.4736
40	0.11273	0.12705	0.14784	0.17349	0.66695	2.0026
30	0.02979	0.0307	0.07864	0.08535	0.56507	1.2992
20	0.00179	0.0018	0.01998	0.02039	0.33547	0.5048
10	0.00000	0.0000	0.00277	0.00278	0.02758	0.0284
0	0.00000	0.0000	0.00000	0.0000	0.00000	0.0000

The initial statistical sums were calculated with allowance for deviations of the rotational component from the classical value.

If the constant depends relatively little on the temperature, values of K for intermediate temperatures can be easily found by linear interpolation. At the highest of the temperatures given (2500°K) the constants are either equal or very close to the classical values given by the factor with the symmetry numbers. For the first, second, and sixth reactions this factor is four, and for the other three it is two. Down to 1000°K, the classical values of the constants are retained for all the reactions except the first.

We write in full the expression for the equilibrium constant for isotopic exchange:

$$H_2 + D_2 \rightleftarrows 2HD;$$

$$K = \frac{[HD]^2}{[H_2][D_2]} = \frac{Z^{0\,2}_{HD}}{Z^0_{H_2} \cdot Z^0_{D_2}} e^{-\Delta E_0/RT}. \tag{154}$$

From Table 24

$$\Delta E_0 = 2E_{0\,HD} - E_{0\,D_2} - E_{0\,H_2} = 157.4 \text{ cal/mole.*}$$

The accuracy of the value of ΔE_0 in Equation (154) is not high, as there are no direct methods for determination of zero-point energies, and different equations for ω_0 and E_0 were used by different authors for their calculation from rotational-vibrational spectra. At the present time E_0 is usually calculated from an approximate equation, the series being broken off at the second term:

---

* This is the arithmetic mean from the two rows of data in Table 20, which give 160 and 154.8 cal/mole respectively.

$$E_0 = \frac{1}{2} hc\omega_e - \frac{1}{4} x_e\omega_e, \tag{155}$$

where ω_e and x_e are the frequency and the anharmonicity coefficient. Unfortunately, values of ω_e and $x_e\omega_e$, which are usually given to 4-5 figures by different authors, differ in the third or sometimes even in the second figure, as can be seen, for example, from the data in Volume 1, Part III, pages 5-6 of the Landolt-Börnstein tables, in which values of ω_0 and $x\omega_0$ for H_2 are given in accordance with Equation (62), and for the other hydrogen molecules ω_e and $x_e\omega_e$ are given in accordance with Equation (155).

TABLE 23

Theoretical Equilibrium Constants for Hydrogen Isotope Exchange, after Zeise [48]

T, °K	Equilibrium constants of reactions					
	$H_2 + T_2 \rightleftarrows 2HT$	$D_2 + T_2 \rightleftarrows 2DT$	$T_2 + HD \rightleftarrows HT + DT$	$H_2 + DT \rightleftarrows HD + HT$	$D_2 + HT \rightleftarrows HD + DT$	$H_2 + D_2 \rightleftarrows 2HD$
2500	3.99	4.00	2.00	1.99	2.00	3.97
2000	3.98	4.00	2.00	1.99	2.00	3.97
1500	3.94	4.00	2.00	1.98	2.00	3.96
1250	3.90	4.00	1.99	1.96	2.01	3.94
1000	3.81	3.99	1.98	1.93	2.02	3.90
900	3.76	3.98	1.97	1.91	2.03	3.87
800	3.68	3.98	1.95	1.88	2.04	3.83
700	3.59	3.97	1.94	1.85	2.05	3.78
600	3.45	3.96	1.91	1.80	2.06	3.72
500	3.26	3.93	1.88	1.74	2.09	3.62
400	2.99	3.88	1.82	1.64	2.13	3.48
300	2.58	3.82	1.74	1.48	2.20	3.26
298.1	2.57	3.82	1.74	1.48	2.20	3.26
250	—	3.77	1.67	—	2.26	—
200	1.948	3.69	1.58	1.24	2.34	2.90
150	—	3.57	1.33	—	2.68	—
100	0.945	3.32	1.18	0.802	2.82	2.26
50	0.242	2.60	0.687	0.353	3.78	1.33
25	—	1.95	0.282	—	6.94	—

Table 24 shows zero-point energy differences for different reactions of molecular hydrogen and reactions between its molecules and atoms, met in the theory of isotopic equilibria

TABLE 24.

Changes of Zero-Point Energy ΔE_0 in Some Reactions of Molecular Hydrogen

Reaction	ΔE_0 per 1 mole	Reaction	ΔE_0 per 1 mole
$H_2 + D_2 \rightarrow 2HD$	+160	$H_2 + D \rightarrow HD + H$ . . .	— 830
$H_2 + T_2 \rightarrow 2HT$	+350	$H_2 + T \rightarrow HT + H$ . . .	—1139
$D_2 + T_2 \rightarrow 2DT$	+ 40	$D_2 + H \rightarrow HD + D$ . . .	+ 990
$HD + T_2 \rightarrow HT + DT$ . . .	+114	$D_2 + T \rightarrow DT + D$	— 384
$HT + D_2 \rightarrow DH + TD$	— 75	$T_2 + H \rightarrow TH + T$	+1489
$DT + H_2 \rightarrow DH + TH$ . . .	+235	$T_2 + D \rightarrow DT + T$	+ 424

TABLE 25

Rotational Energy of Para- and Ortho-Hydrogen and the Heat Effect of the Ortho-Para Conversion at Various Temperatures [49]

T, °K	U_{rot}, cal/mole p-H_2	U_{rot}, cal/mole o-H_2	ΔU, cal/mole o-H_2 − p-H_2
0	0.00	337.17	337.17
15	0.00	337.17	337.17
20	0.00	337.17	337.17
30	0.00	337.17	337.17
40	0.05	337.17	337.12
50	0.20	337.18	336.98
75	5.77	337.22	331.45
100	30.56	338.59	301.03
125	80.09	341.83	261.74
150	146.61	351.40	204.81
175	219.09	368.54	149.45
200	290.22	393.56	103.34
225	357.04	425.69	68.65
250	419.27	463.46	43.19
273.1	473.34	502.16	28.82
298.1	529.12	546.92	17.80

In hydrogen the greatest heats of transition are from forms with even to forms with odd rotation levels.* At low temperatures those heats are of the same order of magnitude as ΔE_0 (compare Tables 25 and 26). Even at T = 0°C $\Delta Q_{p\text{-}H_2 \rightarrow o\text{-}H_2}$ is still approximately 30 cal/mole. This is reflected in the influence of temperature on the thermochemical values and equilibria in the region in which the equilibrium ratio $[o\text{-}A_2]:[p\text{-}A_2]$ differs appreciably from the high-temperature limit.

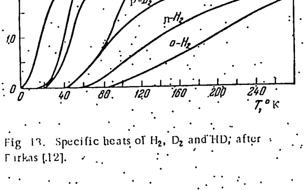


Fig 13. Specific heats of H_2, D_2 and HD; after Farkas [12].

The discrete nature of the levels in conjunction with the relatively high heat effects leads to an unusual course of the heat capacities of homoisotopic hydrogen molecules, as is shown in Fig. 13. In all cases o represents ortho, and p, para molecules; n represents a normal mixture, at equilibrium at the given temperature, of ortho- and para-forms. The existence of the ortho–para transition introduces complications into calculations of isotopic equilibria at low temperatures. The peculiar temperature relationship of the heat capacities is used in analyses of hydrogen mixtures.

Since for hydrogen at low temperatures the rotational sum cannot be replaced by the integral, Equations (94) and (98) of §9 are inapplicable even in the first approximation. Neglecting the mutual influence of vibrations and rotation, insignificant at low temperatures, we must write all the sums separately.

$$Z = g_{el} g_{sp} Z_{tr} Z_{rot} Z_{vibr} =$$

$$= \frac{1}{\sigma} \frac{(2\pi mkT)^{3/2}}{h^3} V \cdot \prod_{i}^{\text{vibr}} \left(1 - e^{-hc\omega_i/kT}\right)^{-1} \sum_{\text{rot}} \qquad (156)$$

---

*For protium and tritium the former are the ortho-forms and the latter the para-forms, and the reverse applies to deuterium.

For HD and HT σ = 1, for H_2, D_2 and T_2 σ = 2

Hence for the reaction $H_2 + D_2 \rightleftharpoons 2HD$

$$K = 4 \frac{m^3_{HD}}{m^{3/2}_{D_2} m^{3/2}_{H_2}} \times$$

$$\times \frac{[\Sigma_{\text{rot}}\ HD]^2 \cdot (1 - e^{-hc\omega_{H_2}/kT})(1 - e^{-hc\omega_{D_2}/kT})}{[\beta_o^H \sum_{\text{rot}} {}_{o\text{-}H_2} + \beta_p^H \sum_{\text{rot}} {}_{p\text{-}H_2}][\beta_o^D \sum_{\text{rot}} {}_{o\text{-}D_2} + \beta_p^D \sum_{\text{rot}} {}_{p\text{-}D_2}](1 - e^{-hc\omega_{HD}/kT})^2} \cdot e^{-160/kT} \qquad (157)$$

It is easy to derive similar equations for the equilibrium constants of all other reactions involving molecular homoisotopic forms of hydrogen

$$D_2 + T_2 \rightleftharpoons 2HT;\ H_2 + D \rightleftharpoons HD + H,$$

etc. In the particular case of exchange of H_2 with D_2, by substituting values of β_o and β_p for H_2 and D_2 from Table 21, values for the rotational sums from Equations (150) and (151), and calculating $u_i = hc\omega/kT$ from the data in Table 5, it is easy to determine K for each temperature. Near room temperatures the corrections are not large, and the rotational statistical sums approximate to integrals; it is therefore more convenient to use the modified Equation (98a) for the separation coefficients

We denote by χ_1 and χ_2 the values of $\frac{hcB}{kT}$ for two molecules differing only in isotopic composition

Multiplication of the right-hand side of Equation (98a) by the series

$$1 + \frac{\chi_1 - \chi_2}{3} + \frac{1}{18}(\chi_1 - \chi_2)^2 + \frac{1}{90}(\chi_1^2 - \chi_2^2) \quad Y_{rot}$$

leads [22] to calculation equations which give a good approximation to the separation coefficients of hydrogen molecules (158)

$$f = [1 + \sum_i \left(\frac{1}{2} + \frac{1}{u_i} - \frac{1}{e^{u_i} - 1}\right)\Delta u_i]\, Y_{rot}. \qquad (158)$$

At low values of the difference $\chi_1 - \chi_2$ it is permissible to stop at three or even two terms in Y_{rot}

At sufficiently high temperatures Y_{rot} tends to zero.

We also give a numerical formula for calculation of K in the temperature range of 200 to 800°K

$$-\log_{10} K = \frac{158}{4.57T} - 0.6276. \qquad (159)$$

Table 26 gives Urey's calculated equilibrium constants for hydrogen exchange between molecular hydrogen and water.

Table 27 is an extract from Table 26 for 3 reactions, with values of ΔE_0:

Table 27 shows that even at 600°K the values of K for all three reactions do not differ greatly from the classical value. For the first reaction ($H_2O + D_2O \rightleftharpoons 2HDO$), which occurs with the least change of zero-point energy (ΔE_0 = 37 cal/mole) K is close to the classical value even at 0°C. The deviations for the other two reactions at 0°C are about 20%, and they are greater for the second, which has the highest value of ΔE_0. This is yet another illustration of the importance of change of zero-point energy as the main quantity which determines deviations of K from the classical values. Unfortunately, as was pointed out earlier, despite the high accuracy of spectroscopic determinations, the values of E_0 and therefore of ΔE_0 are in many cases found from these determinations without sufficient accuracy or certainty. Table 28 gives additional examples of equilibrium constants for isotopic exchange of protium with deuterium at 25°C. Tables 23 and 26 show that with increase of temperature the equilibrium constants tend smoothly to the ideal values, corresponding to the ratio of the reciprocal symmetry numbers of the molecules participating in the equilibrium. This K_{id} is most often 1, and some-

TABLE 26

Equilibrium Constants for Exchange Between Hydrogen and Water, After Urey [21]

Equilibrium	0°	273.1° K	298.1° K	400° K	500° K	600° K
$\frac{[HD]^2}{[H_2][D_2]}$	0	3.18	3.25	3.48	3.62	3.72
$\frac{[HDO]^2}{[H_2O][D_2O]}$	0	3.94	3.96	4.00	4.02	4.03
$\frac{[HDO][H_2]}{[H_2O][HD]}$	∞	4.29	3.70	2.46	1.94	1.66
$\frac{[D_2O][HD]}{[HDO][D_2]}$	∞	3.46	3.05	2.14	1.75	1.53
$\frac{[HT]^2}{[H_2][T_2]}$	0	2.42	2.56	2.97	3.24	3.44
$\frac{[HTO]^2}{[H_2O][T_2O]}$	0	3.34	3.42	3.03	3.74	3.80
$\frac{[HTO][H_2]}{[H_2O][HT]}$	∞	7.64	6.19	3.46	2.47	1.99
$\frac{[T_2O][HT]}{[HTO][T_2]}$	∞	5.54	4.63	2.84	2.15	1.80
$\frac{[DT]^2}{[D_2][T_2]}$	0	3.59	3.82	3.88	3.92	3.94
$\frac{[DTO]^2}{[D_2O][T_2O]}$	0	3.55	3.59	3.70	3.76	3.80
$\frac{[DTO][D_2]}{[D_2O][DT]}$	∞	1.63	1.55	1.34	1.23	1.16
$\frac{[T_2O][DT]}{[DTO][T_2]}$	∞	1.75	1.65	1.40	1.28	1.21

TABLE 27

Equilibrium Constants for Hydrogen Exchange of Water, After Zeise [48]

Equilibrium	Equilibrium constants at temperature, °K					ΔF_0, cal/mole
	273.1	298.1	400	500	600	
$\frac{[HDO]^2}{[H_2O][D_2O]}$	3.94	3.96	4.00	4.02	4.03	+.37
$\frac{[HTO]^2}{[H_2O][T_2O]}$	3.34	3.42	3.63	3.74	3.80	+153
$\frac{[TDO]^2}{[D_2O][T_2O]}$	3.55	3.59	3.70	3.76	3.80	+ 72

times 4 or 2. However, in some cases the dependence of K on temperature is more complex. For example, for the reaction

$$H_2 + 2DI \rightleftharpoons D_2 + 2HI \qquad (160)$$

the value of K passes through a maximum.

TABLE 28

Examples of Equilibrium Constants of Isotopic Exchange of Protium with Deuterium for Some Inorganic Hydrides

System	K	T, °K
$HCl + DBr \rightleftharpoons DCl + HBr$ gas	1.220	298
$HCl + DI \rightleftharpoons HI + DCl$ gas	1.537	298
$HCl + \frac{1}{2} D_2 \rightleftharpoons DCl + \frac{1}{2} H_2$ gas	1.420	298
$\frac{1}{2} H_2 + NaD \rightleftharpoons NaH + \frac{1}{2} D_2$	2.360	298
$PH_2D + H_2O \rightleftharpoons PH_3 + DHO$ gas	1.52	298
$PH_2D + H_2O \rightleftharpoons PH_3 + DHO$ solution	1.63	298

It is instructive to compare the values of Q_2/Q_1 and K for hydrogen and non-hydrogen equilibria (Tables 10, 14, 41). For C, O, N Q_2/Q_1, even at 273.1 and 298°K, exceed unity by some hundredths, more rarely by 1-2 tenths, and tend to 1 at high temperatures. The isotopic exchange equilibrium constants, as a rule, differ still less from 1. In contrast to this, the ratio of the statistical sums for hydrogen and its compounds at 0°C and room temperature can considerably exceed unity. For example, at 0°C the ratio for LiD/LiH = 1.8604, for DCl/HCl = 6.3726, and for $(D_2O/H_2O)^{1/2}$ = even 16.467. Similarly, the isotopic exchange equilibrium constants can differ very considerably from the ideal values corresponding to the symmetry number ratios. For example, at 273.1°K for the reaction $DI + HCl \rightleftharpoons DCl + HI$, K = 1.586, for the reaction $2LiD + H_2O \rightarrow 2LiH + D_2O$, K = 8.851, for the reaction $KD + HBr \rightarrow KH + DBr$, K = 3.408, etc. The values of Q_2/Q_1 and K also depend more sharply on the temperature.

c) Hydrogen compounds

Isotopic equilibria of hydrogen compounds have been intensively studied since the discovery of deuterium, i.e., for more than 30 years [12], [20]. The bulk of the data is on the exchange of protium with deuterium, but during the past 5-6 years fairly extensive material has also been collected on equilibria of protium – tritium exchange. In view of the great practical importance of the exchange reactions of hydrogen in the production of heavy water and tritium oxide, the calculation methods were developed with reference to the specific characteristics of hydrogen, and for a long time the theory of isotopic equilibria was developed with considerable emphasis on hydrogen.

The equilibria for the exchange of molecular hydrogen with water, ammonia, hydrogen sulfide, and halides have been experimentally studied in detail. Equilibria of isotopic exchange of different forms of water and ammonia with each other and of hydrogen exchange between its various binary compounds have been studied. Detailed numerical data on the starting values of the statistical sums and equilibrium constants for 28 exchange reactions of stable hydrogen compounds are given in Urey's summary table [21], which is included in Section II of the Appendix. This table is compiled on the same principle as the same author's tables for carbon. Tables for certain exchange reactions of atomic hydrogen are also given. As an indication of the order of magnitude of the values found, Tables 26 and 28 give a selection of data on the equilibrium constants of the simplest molecules.

§17. Distribution Coefficients of Hydrogen Isotopes Between Hydrides and Their Dependence on the Positions of the Elements in D.I. Mendeleev's Periodic Table

An interesting paper was recently published by Ya.M. Varshavsky and S.E. Vaisberg [50] on the laws of deuterium distribution in the isotopic exchange of hydrogen.

Using the statistical equations given in §5-7 of this chapter, the authors performed a detailed theoretical analysis of the values of the distribution coefficients of deuterium between a large number of hydrides, and

TABLE 29

Calculation of Distribution Coefficients α of Deuterium, for Different Hydrides [50]

Substance	*a*	*b*	β_{20° C	β_{50° C	β_{75° C	Distribution coefficients, $\alpha_{20^\circ C}$														
						H_2	CH_4	C_2H_6	C_2H_4	C_6H_6	NH_3	H_2O	HF	PH_3	H_2S	HCl	AsH_3	H_2Se	HBr	HI
H_2	0.8484	418.7	3.54	3.10	2.83	1	0.329	0.316	0.812	0.298	0.303	0.305	0.364	0.615	0.649	0.693	0.752	0.801	0.843	1.05
CH_4	0.5071	894.5	10.74	8.04	6.63	3.04	1	0.959	0.947	0.904	0.920	0.924	1.10	1.87	1.97	2.10	2.28	2.43	2.56	3.18
C_2H_6	0.4640	932.8	11.20	8.33	6.77	3.16	1.04	1	0.988	0.943	0.959	0.964	1.15	1.94	2.05	2.19	2.38	2.53	2.67	3.31
C_2H_4	0.4632	936.8	11.33	8.42	6.84	3.20	1.05	1.01	1	0.953	0.970	0.975	1.16	1.97	2.08	2.22	2.41	2.56	2.70	3.35
C_6H_6	0.4128	984.7	11.89	8.70	6.99	3.36	1.11	1.06	1.05	1	1.02	1.02	1.22	2.06	2.18	2.33	2.52	2.69	2.83	3.52
NH_3	0.5611	889.4	11.68	8.81	7.23	3.30	1.09	1.04	1.03	0.982	1	1.01	1.20	2.03	2.14	2.29	2.48	2.64	2.78	3.46
H_2O	0.6344	852.1	11.62	8.87	7.34	3.28	1.08	1.04	1.02	0.978	0.995	1	1.19	2.02	2.13	2.28	2.47	2.63	2.77	3.44
HF	0.7340	757.3	9.73	7.66	6.47	2.75	0.905	0.868	0.857	0.818	0.832	0.837	1	1.69	1.78	1.90	2.06	2.20	2.32	2.88
PH_3	0.5337	696.8	5.76	4.62	3.95	1.62	0.536	0.514	0.508	0.484	0.493	0.496	0.592	1	1.05	1.13	1.22	1.30	1.37	1.70
H_2S	0.6291	633.1	5.46	4.47	3.88	1.54	0.508	0.487	0.481	0.459	0.467	0.470	0.561	0.948	1	1.07	1.16	1.23	1.30	1.57
HCl	0.7245	572.1	5.11	4.26	3.75	1.45	0.476	0.456	0.451	0.430	0.438	0.440	0.525	0.888	0.936	1	1.09	1.16	1.22	1.51
AsH_3	0.5312	639.3	4.71	3.85	3.34	1.33	0.438	0.420	0.415	0.396	0.403	0.405	0.484	0.817	0.863	0.922	1	1.06	1.12	1.39
H_2Se	0.6099	580.2	4.42	3.68	3.23	1.25	0.411	0.395	0.390	0.372	0.378	0.381	0.445	0.768	0.810	0.866	0.939	1	1.05	1.31
HBr	0.7192	517.3	4.20	3.57	3.18	1.19	0.391	0.375	0.371	0.353	0.359	0.362	0.432	0.729	0.770	0.822	0.891	0.950	1	1.24
HJ	0.7178	453.7	3.38	2.93	2.64	0.955	0.315	0.302	0.298	0.284	0.289	0.291	0.347	0.587	0.619	0.661	0.717	0.764	0.805	1

TABLE 30

Vibrational Frequencies of Various Hydrides and Deuterides [50]

Molecule	H_2	CH_4	C_2H_6	C_2H_4			C_6H_6			NH_3	PH_3	AsH_3	H_2O	H_2S	H_2Se	HF	HCl	HBr	HI
Observed fundamental frequency, cm^{-1}	4154.65	1306.2 1306.2 1306.2 1526 1526 2914.2 3020.3 3020.3 3020.3	275 820.8 820.8 993 1155 1155 1375 1379.0 1460 1460	1486.0 1486.0 2899.2 2954 2963 2963 2994.3 2994.3	825 943 949.2 995 1050. 1342.4 1443.5 1623.3 2989.5 3019.3	3105.5 3272.3	405 405 606 606 671 703 849. 849 970 970	985 992 1010 1037 1037 1110 1178 1178 1326 1485	1485 1596 1596 1648 3047 3047 3060 3062 3080 3080	950 1627.5 1627.5 3336 3414 3414	990 1121.4 1121.4 2327 2421 2421	906 1005 1005 2122 2185 2185	1595.0 3651.7 3755.8	1290 2610.8 2684	1074 2260 2350	3958.4	2885.7	2559.3	2230.1

Molecule	D_2	CD_4	C_2D_6		C_2D_4		C_6D_6			ND_3	PD_3	AsD_3	D_2O	D_2S	D_2Se	DF	DCl	DBr	DI
Observed fundamental frequency, cm^{-1}	2990.5	995.6 995.6 995.6 1054 1054 2084.7 2258.2 2258.2 2258.2	200 601 601 852 970 970 1158 1055 1055 1072	1102 1102 2083 2111 2225 2225 2236 2236	580 712 720 780 883 981 1077.9 1515 2200.2 2251	2304 2345	352 352 496 577 577 601 662 662 793 793	813 813 825 827 867 867 943 963 1037 1333	1333 1551 1551 1571 2265 2265 2290 2293 2294 2294	749 1191 1191 2420 2555 2555	730. 806 806 1694 1730 1730	660 714 714 1534 1560 1560	1178.7 2666 2789	934 1891.6 1999	745 1630 1696	2905.7	2090.4	1840.2	1599.4

correlated the results with the positions of the elements forming the hydrides in the periodic system. Their distribution coefficient $\alpha = \frac{[D]/[H]_1}{[D]/[H]_2}$ is equivalent to our coefficient f. Applying the simplifications usual in isotope chemistry in expressing the statistical sums, and neglecting the influence of deutero-substitution of the molecule on the equilibrium constants K and on f, they were able, for characterization of exchange between molecules of any degree of substitution, to use the equilibrium constant for the aggregate reaction

$$mAH_n + nBD_m \rightleftharpoons mAD_n + nBH_m, \tag{161}$$

and

$$f = \sqrt[nm]{K}. \tag{162}$$

It was further shown that, on certain assumptions, α = f may be expressed as the ratio of the functions β_1 and β_2, which they term the β-factors. These represent the degree of nonequivalence of the hydrogen isotopes with respect to a definite element in a given compound.

$$\alpha = \frac{\beta_1}{\beta_2}. \tag{163}$$

The value of the β-factor for a given compound may be written as

$$\beta = ae^{bT}. \tag{164}$$

Table 29 shows values of a and b for various binary hydrides, and values of β calculated from them at three temperatures and of α at 20°C. Table 30 gives the vibrational frequencies used for the calculation. The authors draw attention to the small variations of β between neighboring saturated hydrides of the same series of the periodic system, and the sharp changes in the transition to neighboring elements of the same group. This is explained by the decisive influence of the mass of the atom combined with hydrogen A different picture is seen on comparing hydrides with one hydrogen atom for different elements. Here saturated hydrides (HF, NaH, etc.) are compared with radicals (OH, NH, etc.). It is seen from Fig. 14, which is based on Table 31, that the values of β show a fairly distinct periodicity.

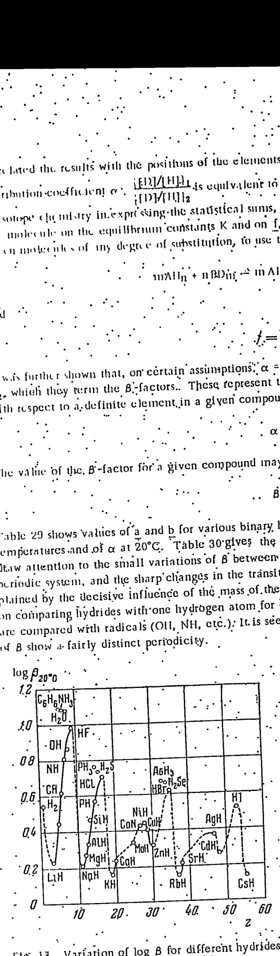


Fig. 14. Variation of log β for different hydrides with the atomic number of the element combined with hydrogen [50].

As a first attempt to establish a general form of relationship between the elementary composition of exchanging hydrogen compounds and the magnitude of the thermodynamic isotope effects, the work of Varshavsky and Vaisberg is important in principle.

§18. Calculations of Isotope Effects with the Aid of Computer Techniques

Until recently the principal attention in the theory of thermodynamic isotope effects has been devoted to the search for approximate solutions. As a result, functions and equations were derived which could be used to calculate, without great expenditure of time, the magnitudes of the corresponding corrections, using a small number of substantive characteristics of the given substance.

Development in this direction cannot be regarded as completed, and its inherent potentialities have not been fully utilized. However, recently a new and highly promising route for determination of isotopic corrections has appeared, based on the use of electronic computers. The search for approximate solutions, based on simplified rational and empirical formulas, was largely motivated by the laborious nature of calculations with the aid of more exact equations. For these reasons, the complete equations for rotational-vibrational systems were for the most part replaced by separate equations for rotation and vibration, independent rotational and vibrational sums; in the form of various simplified functions, were introduced into the general equations for Γ, S, U, and K. Many complex calculations can be performed with great ease with the aid of modern computers, and various mathematical operations can be performed with expenditure of very little time With a suitable choice of the initial equations this makes searches for approximate methods unnecessary

The only condition is the availability of reliable quantitative data. As was shown in Sections 6 and 7 of this chapter, because of the similarity of properties of isotopic molecules the number of data needed for calculations of isotopic equilibria is far less than for calculations of ordinary elementary equilibria. Often all the initial data are available, and there are no obstacles to utilization of the advantages of computer techniques. Therefore there is reason to expect extensive development in a new direction in the theoretical chemistry of isotopes. As yet it is represented by a small number of investigations performed by the American Bureau of Standards. We give here a brief account of one of these; published in December, 1954, and devoted to the thermodynamical properties of isotopic forms of water [51a].

TABLE 31*

Values of the Frequencies β and log β for Various Hydrides and Deuterides with One Hydrogen Atom in the Molecule [50]

Atomic number	Element	Frequency of hydride, cm^{-1}	Frequency of deuteride, cm^{-1}	$\beta_{20°C}$	$\log\beta_{20°C}$
1	H	4154.65	2990 5	3.54	0.549
3	Li	1359.2	1028 7	1 72	0.234
5	B	2268	(1730)	2.82	0.450
6	C	2732	2023	4.22	0.625
7	N	(3300)	[2410]	6.50	0 812
8	O	3571.6	2632.7	7.40	0 868
9	F	3958.4	2905.7	9.73	0 988
11	Na	1132.8	(806)	1.64	0.215
12	Mg	1432.9	1045.6	1 90	0.279
13	Al	1624.3	1181.6	2.17	0.335
14	Si	(2080)	[1496]	3.03	0 480
15	P	2380	[1709]	3.73	0.571
17	Cl	2885.7	2090.4	5.11	0.708
19	K	964.5	[690.5]	1.45	0.162
20	Ca	1260	[902]	1.75	0.241
25	Mn	(1580)	[1127]	2.18	0.339
27	Co	(1890)	[1348]	2.71	0.432
28	Ni	(1926.6)	[1374]	2.77	0 443
29	Cu	1866.0	1346.1	2.59	0 413
30	Zn	1497.3	[1966.7]	2.06	0.314
35	Br	2559.3	1840.2	4.20	0.624
37	Rb	908.5	[646.1]	1.41	0.148
38	Sr	1172.2	[833.5]	1.66	0.220
47	Ag	1691.9	[1201.8]	2.37	0.375
48	Cd	1338 1	[950.4]	1.86	0.269
53	I	2230 1	1599.4	3 38	0.528
55	Cs	875.5	[621.4]	1.38	0.141

---

*Round parentheses show frequencies known with less accuracy; the square parentheses show frequencies of the deuterides calculated from the frequencies of the deuterides calculated from the frequencies of the corresponding hydrides, using the reduced masses of these hydrides and deuterides.

Despite the simplicity of the water molecule, its rotational-vibrational spectra are relatively complex because of its nonlinear character. In calculations of equilibrium constants it is also necessary to take into consideration differences in the symmetry numbers of molecules mono- and diisotopic with respect to hydrogen. In the investigation in question, the authors calculated the initial thermodynamic quantities for all the hydrogen isomers of the water molecule, i.e., for H_2O, HDO, D_2O, HTO, T_2O and DTO. The calculation covered an enormous temperature range from 50 to 5000°K. Enthalpies, thermodynamic potentials, entropies, and heat capacities at constant pressure were calculated. The results of these calculations are contained in tables, which are given in the Appendix in this book. The calculations were based on new data on the molecular constants for water determined from infrared spectra. The statistical sums were calculated from equations containing corrections which are usually neglected in calculations performed "by hand." Thus, corrections were applied for anharmonicity of vibrations, for rotational-vibrational interaction, and for centrifugal extension. At low temperatures additional correction terms were introduced into the expressions for the rotational sums. The thermodynamic functions were expressed in terms of such sums, coded, and the computer gave complete tabular data for all four thermodynamic functions for the given molecule in a few minutes. In a later paper the same authors published the results of machine computation of tables of the same type for several isotopic radicals: OH, OD, OT, SH, SD and ST. In this case the original equations were still more complex because, in addition to rotational-vibrational interaction, rotational bond extension, and anharmonicity, corrections were also applied for the electronic characteristics of the initial level for these radicals [51]. Some of these data are also given in the Appendix. The authors mention the use of the same technique for calculation of thermodynamic functions of isotopic forms of other hydrides and of isotopic exchange equilibria. Months of work would be required for calculation, from these equations, of all 40 values of any one thermodynamic value for one isotopic substance. Verification of individual points by the usual method showed that the results were completely reliable. The only significant simplification in the work was that the calculations were made for an ideal gas. The results are therefore directly applicable only to water vapor. Moreover, at low temperatures this vapor must be highly rarefied. This assumption does not introduce any large limitations into the calculation of isotopic equilibria for non-ideal vapors, as the deviations from ideality, represented by activity coefficients, are practically the same for different isotopic forms. The results obtained are not directly applicable to crystalline and liquid water, but since at equilibrium the chemical potentials of a substance present in different phases are equal, it is possible, with a knowledge of vapor pressures, to determine the thermodynamic characteristics of water in condensed states. There are no obstacles in principle to the use of computer techniques for calculations of thermodynamic data for non-ideal systems. The enormous output of computers in calculations of thermodynamic characteristics of isotopic substances gives reason to expect the appearance, in the near future, of similar detailed tables of thermodynamic functions of most ordinary substances. These will then be used for completing and improving tables of separation functions, and detailed and reliable data on equilibrium constants and thermal effects of isotopic reactions will be rapidly accumulated. In this optimistic appraisal of the prospects of the use of computer techniques in the theory of isotopic thermodynamic effects, it must nevertheless be remembered that while computer techniques radically shorten the time and labor required for compilation of tables based on available formulas, they do not remove the need for derivation of such formulas, but involve additional, sometimes fairly laborious transformations for obtaining the data in the coded form required for the computers. Numerous exact experimental determinations of the numerical constants entering the original expressions become necessary. Therefore the need for experimental determinations and preliminary analysis of the results will not diminish but increase with the use of high-speed computers.

§ 19 Experimental Verification of the Statistical Theory of Isotope Effects

The physical principles of the statistical theory of isotope effects arouse no doubts. Spectroscopic determinations used for determinations of the numerical data on the individual properties of real systems are reliable and exact. Probably for this reason the number of systematic verifications of the theory is not large. As a rule, in experimental determinations of isotopic equilibrium constants and thermodynamic isotope effects the results of the spectroscopic statistical theory are accepted without reservation, and the problem is restricted to determinations of numerical values of these constants for systems for which they cannot, for one reason or another, be calculated with sufficient accuracy.

In §9 we drew attention to the great merits of the Bigeleisen–Mayer approximate equations, which were first proposed in 1949 and augmented by tabulated values of the G(u) function in 1953. By that time the results of the principal special studies on the comparison of theoretical and experimental values of K had been published, while for most of the simpler molecules detailed calculations of the statistical sums termed partition functions by the Anglo-American scientists, were available, based on the more complete but also more cumbersome equations of Urey, Libby, Kassel, and others. Therefore the theoretical constants used below for comparison with experimental data were obtained not with the aid of the Bigeleisen – Mayer equations, but with the use of earlier equations of other authors.

This is to some extent justified by the choice, as examples, of processes of hydrogen exchange, for which the use of less rough approximations, and, accordingly, of more complex equations, is justified. At the same time, owing to the higher absolute values of the isotopic corrections, the accuracy of their experimental determinations is higher than for exchange of other elements.

a) Gaseous reactions.

Both the approximate and the exact equations of the spectroscopic statistical theory of isotopic thermodynamic effects are directly applicable only to gaseous systems close to ideality. Therefore, for verification of the theory the results of measurements on gaseous reactions are of primary importance. We will begin with the equilibrium for the isotopic exchange of protium with deuterium, which is one of the simplest and best studied isotopic exchange reactions

$$H_2 + D_2 \rightleftharpoons 2HD.$$

The calculated values of the initial statistical sums and separation coefficients for this reaction are given in tables in the Appendix, and the zero-point energies in Table 20.

The first measurements of the equilibrium constants were performed by the brothers Farkas [11]. These results were later obtained with greater precision by other authors. As a rule, catalysts were introduced into the system to bring about a state of equilibrium quickly; as was noted earlier, catalysts do not influence the magnitude of isotope effects.

Two values for ΔE_0 for this reaction can be obtained from Tables 24 and 20: 160 cal/mole from [illegible] data, and 254.2 cal/mole from Clusius's data. The first of these is near to 158.2 cal/mole, used in individual publications and in the Farkas monograph. With the use of this value and with consideration of the symmetry numbers, the expression for the equilibrium constant assumes the form:

$$K = 4\,e^{-70.1/T}. \qquad (165)$$

Rotational corrections are ignored.

Table 32 gives experimental values of K, and values of K calculated by Fowler and Guggenheim from the very similar equation

$$K = 4 \cdot 1.06 \cdot e^{-78/T}. \qquad (165a)$$

TABLE 32

Comparison of Equilibrium Constants for Isotopic Exchange of H_2 with D_2, Determined Experimentally and Calculated from Equation (165a)

T, °K	195	273	298	383	543	670	741
K_{exp}	2.92	3.24	3.28	3.50	3.85	3.8[illegible]	3.70
Deviations	±0.08	±0.08	–	±0.06	±0.10	±0.[illegible]4	±0.12
K_{calc} (from 165a)	2.84	3.18	3.26	3.46	3.67	3.77	3.81

We shall give in greater detail the derivation of Equation (165a), which differs somewhat from those considered earlier. The initial general equation for the equilibrium constant of isotopic exchange of diatomic molecules as applied to the exchange of H_2 with D_2 has, on the basis of Equation (154), the form

$$K=\frac{Z^{3}_{tr\,HD}Z^{2}_{rot\,HD}Z^{02}_{vibr\,HD}\sigma_{D_2}\sigma_{H_2}g^{2}_{el\,HD}g^{2}_{sp\,HD}}{Z_{tr\,H_2}Z_{tr\,D_2}Z_{rot\,H_2}Z_{rot\,D_2}Z^{0}_{vibr\,H_2}Z^{0}_{vibr\,D_2}\sigma^{2}_{HD}g_{el\,H_2}g_{el\,D_2}g_{sp\,H_2}g_{sp\,D_2}}\cdot e^{-(2E_{0HD}-E_{0H_2}-E_{0D_2})/kT} \tag{154a}$$

We denote the masses of H and D by m_H and m_D; then, from (43a)

$$\frac{Z^2_{HD}}{Z_{H_2}Z_{D_2}}\ \text{tr} \approx \left(\frac{m_H+m_D}{2m_H^{1/2}m_D^{1/2}}\right)^3;$$

for classical rotation

$$\frac{Z^2_{HD}}{Z_{H_2}Z_{D_2}}\ \text{rot.} = \frac{I^2_{HD}}{I_{H_2}I_{D_2}},$$

where I is the moment of inertia, taking

$$\frac{Z^{02}_{HD}}{Z^0_{H_2}Z^0_{D_2}}\ \text{vibr} \begin{array}{ll} \nearrow\ 1 & (\text{when } h\nu \gg kT) \\ \searrow\ \dfrac{\omega_{H_2}\omega_{D_2}}{\omega^2_{HD}} & (\text{when } kT \gg h\nu).^* \end{array}$$

Since the electronic states are identical for all three types of molecules and for the nuclear statistical weights, determined by the orientation of the nuclear spins, the fraction $\Pi g_{sp} \cdot g_{el} = 1$, the symmetry numbers for H_2 and D_2 = 2, and for HD = 1, and therefore

$$\frac{\sigma_{H_2}\cdot\sigma_{D_2}}{\sigma_{HD}} = 4.$$

With these simplifications, when $kT \gg h\nu$ the equation takes the form

$$K = 4\left(\frac{m_H+m_D}{2m_H^{1/2}\cdot m_D^{1/2}}\right)^3 \frac{I^2_{HD}}{I_{H_2}I_{D_2}}\cdot e^{-\Delta E_0/kT} \tag{154b}$$

Assuming that the interatomic forces and r_0 are independent of the atomic masses, (48) and (56a) can be used to express the ratios of I and ω in terms of these masses

$$I_{H_2} : I_{D_2} : I_{HD} = m_H : m_D : \frac{2m_H\cdot m_D}{m_H+m_D} \tag{166}$$

$$\omega_{H_2} : \omega_{D_2} : \omega_{HD} = m_{H_2}^{-1/2} : m_{D_2}^{-1/2} : \left(\frac{2m_H\cdot m_D}{m_H+m_D}\right)^{-1/2} \tag{166a}$$

From (166), the fraction $\frac{I^2_{HD}}{I_{H_2}I_{D_2}}$ becomes $\left(\frac{2m_H^{1/2}m_D^{1/2}}{m_H+m_D}\right)^2$.

Equation (166a) makes it possible to replace the algebraic sum of three independent E_0, each calculated from its fundamental frequency

$$2E_{0HD} - E_{0H_2} - E_{0D_2} = \frac{1}{2}Nh(2\nu_{HD} - \nu_{H_2} - \nu_{D_2}) =$$
$$= \frac{1}{2}Nhc(\omega_{HD} - \omega_{H_2} - \omega_{D_2}),$$

---

* This corresponds to Tatevsky's approximation (see §9).

by an expression containing only one such frequency, for example ω_{HD}. This gives (167)

$$2E_{0HD} - E_{0H_2} - E_{0D_2} = Nh\omega\left\{1 - \frac{\frac{1}{2}(m_H^{1/2}+m_D^{1/2})}{\left(\frac{1}{2}m_H+\frac{1}{2}m_D\right)^{1/2}}\right\} \tag{167}$$

The final expression for K takes the form

$$K = 4\left(\frac{m_H+m_D}{2m_H^{1/2}m_D^{1/2}}\right)\exp\left\{-\frac{h\omega_{HD}}{kT}\left[1-\frac{\frac{1}{2}(m_H^{1/2}+m_D^{1/2})}{\left(\frac{1}{2}m_H+\frac{1}{2}m_D\right)^{1/2}}\right]\right\} \tag{167a}$$

The value of the fraction in parentheses is 1.06, while the exponent at ν_{HD} = 3770 cm^{-1} is found to be equal to $-\frac{78}{T}$.

Table 32 shows how well such a formula, based on the assumption of classical rotation of hydrogen molecules, and involving, in addition to the ratio of the isotope masses, only one fundamental frequency, agrees with the experimental results. We may note that the fundamental frequency of the molecules of ordinary hydrogen H_2 could have been used as the original frequency.

Examination of the table shows that even at 195°K, i.e., at −78°C, the error which results from neglect of the deviation of Z_{rot} from the classical value is not large, being only about 3%. Calculation with the use of complete rotational sums would have given K = 2.87 and thus would have decreased the deviation to 1.8%.

At a lower temperature, comparison with Equation (165a) would have shown considerable deviations from the experimental data. However, in this instance comparison of the experimental data with the values of the constants calculated from the more complete equation demonstrates the complete reliability of the statistical theory.

Many experimental investigations have dealt with equilibria of reactions of interest for the enrichment and extraction of deuterium. Among gaseous reactions of this type is the isotopic exchange between water vapor and hydrogen. Let us consider the results of a comparison of experimentally determined and theoretical equilibrium constants for the reaction $H_2O + HD \rightleftharpoons HDO + H_2$. K was calculated from the formula

$$K = \frac{Q_{HDO}Q_{H_2}}{Q_{H_2O}Q_{HD}} \tag{168}$$

with consideration of anharmonicity of vibration and of rotational sums. The constants for H_2 and HD used in the calculations are given in Table 33, which, for completeness, also gives data for D_2. Tables 34 and 35 give the constants for the isotopic forms of water, used in the calculations.

The complete statistical sum for any of the water molecules has the form

$$Q = \left(\frac{2\pi MkT}{Nh^2}\right)^{3/2}\frac{1}{\sigma}\sum_{n_1;\,n_2;\,n_3}\frac{8\pi^2(8\pi^3 I_A I_B I_C)^{1/2}kT^{3/2}}{h^3}\exp\left[-\frac{E(n_1;n_2;n_3)}{kT}\right], \tag{169}$$

where n_1, n_2, and n_3 are quantum numbers corresponding to three normal vibrations of the molecules (see §7). In view of the high value of ω, excitation of the first level only is considered, and the summation is performed directly.

Table 36 gives calculated ratios of the distribution functions for the isotopic molecules involved in the equilibrium under consideration at the experimental temperatures.

These data were used to calculate the equilibrium constants, given in Tables 37 and 38.

Table 38 gives a comparison of the theoretical results with the experimental data of some authors.

At first sight the data in Table 37 appear contradictory and the agreement poor. It is easy to see, however, that the greatest discrepancies between theory and experiment are mainly found for the earlier work, performed without elimination of certain specific sources of experimental error typical of this process. The

TABLE 33

Constants of Isotopic Molecules of Hydrogen as Used in the Calculations, after Kirshenbaum [44]

Constant	H_2	HD	D_2
Mol. wt. ($O^{16} = 16{,}000$)	2,01556	3,02131	4,02706
$B_0 = \frac{h}{8\pi^2 I_0 c}$, cm^{-1}	59.309	44.655	29.913
$E_0/hc = \frac{1}{2}\omega_0$, cm^{-1}	2171.4	1884.3	1542.4
$4\gamma^2\left(-\frac{D_e}{B_e}\right)$	0.000764	0.000574	0.000381
Symmetry number	2	1	2

TABLE 34

Vibrational Frequencies of Isotopic Forms of Water, after Kirshenbaum [44]

	Fundamental frequency cm^{-1}		
	H_2O	HDO	D_2O
Fundamental frequencies			
ω_1	3825.03	2818.46	2757.85
ω_2	1653.78	1449.55	1212.17
ω_3	3935.32	3882.53	2883.48
Anharmonicity corrections			
X_{11}	− 43.89	− 23.82	−22.81
X_{22}	− 19.50	− 14.98	−10.44
X_{33}	− 46.37	− 45.14	−24.90
X_{12}	− 20.02	− 12.93	−10.56
X_{13}	−155.06	−112.72	−81.92
X_{23}	− 19.81	− 17.13	−10.62

data of the most careful determinations, in which the possible error was estimated, are, on the contrary, in good agreement with theory. Good agreement with theory was also found for the less well studied isotopic exchange between water and hydrogen involving tritium [52].

As a third example, we consider the isotopic exchange of light ammonia with HD molecules

$$NH_3 + HD \rightleftharpoons NH_2D + H_2.$$

For this reaction, as for other exchange reactions of ammonia, detailed calculations of the equilibrium constants are available, with detailed consideration of the molecular structure. Table 39 gives the results of a comparison, made by Herrick and Sabi,* of experimental and theoretical data.

TABLE 35

Rotational Constants for Isotopic Forms of Water,* after Kirshenbaum [44]

Constant	H_2O	HDO	D_2O
I_A^0	0.611747	0 724769	1.009682
α_1	+0.0211	+0.0155	+0.0152
α_2	−0.1003	−0.0870	−0.0734
α_3	+0.0482	+0.0475	+0 0353
I_B^0	1.153128	1.842200	2.304505
β_1	+0.0206	+0.0152	+0 0140
β_2	−0.0120	−0.0113	−0.0094
β_3	+0.0040	+0.0030	+0.0029
I_C^0	1.764875	2.566978	3 404187
γ_1	+0.0203	+0.0150	+0.0146
γ_2	+0.0128	+0.0112	+0.0094
γ_3	+0 0146	+0 0144	+0 0107
n_s (symmetry number)	2	1	2

---

*α, β, γ are coefficients in the equation for the moments of inertia as functions of the quantum numbers.

TABLE 36

Calculated Values of the Statistical Sums, after Kirshenbaum

T, °C	Q_{HD}/Q_{H_2}	Q_{HDO}/Q_{H_2O}
0	21 5968	90.402
25	19.0597	68.982
50	17.1511	54.890
75	15 6676	45.134
100	14.4882	38.0975
125	13.5294	32 8484

TABLE 37

Theoretical Values of the Equilibrium Constant for the Reaction $H_2O + HD \rightleftharpoons HDO + H_2$ in the Gas Phase*

T, °C	K	T, °C	K
0	4.19	75	2 88
20	(3 78)	100	2 63 (2 65)
25	3.62	125	2.43
47.5	3.25	200	(2 09)
50	3.20	300	(1 75)
		500	1 37

---

*Data given without parentheses are those of Kimball and Stockmayer, those in parentheses, of Libby (see Kirshenbaum [44]).

Each of the experimental values in the table represents the average from two or more experiments. The absence of false equilibria was confirmed by agreement between values obtained on approaching equilibrium from opposite directions. In view of the difficulty of such determinations, the deviations between the experimental and the theoretical values must be regarded as small. Moreover, they were not of a systematic character, as is seen from the K−T graph (Fig. 15). (See also Section II of the Appendix.)

In §16 we noted the peculiar nature of the deductions from the statistical theory for the isotopic equilibrium of hydrogen iodide with deuterium. The equilibrium constant should pass through a maximum at a temperature of the order of 600°K. Fig. 16 shows Blagg and Murphy's [53] expected theoretical course of K in the temperature range from 300 to 1500°. The value of $K_{id} = 1$, as the products of the symmetry numbers of the molecules both in the left and in the right-hand side of Equation (160) are $\frac{1}{2}$ The theoretically calculated values were confirmed experimentally over limited ranges of temperature It has not yet proved possible to reproduce the theoretical curve completely.

---

*Cited from Kirshenbaum [44].

TABLE 38

Comparison of Experimental and Theoretical Values for the Reaction $H_2O + HD \rightleftharpoons HDO + H_2$ in the Gas Phase, after Kirshenbaum [44]

T, °C	Equilibrium constants		Authors of experimental work
	theoretical	experimental	
20	3 78	2 67	Farkas
25	3.62	3.88 ± 0.05	Grosse
47.5	3 25	3.20 ± 0.15	Herrick, Kirshenbaum and Brown
56 5	3.12	3.13	Taylor et al.
80.0	2 83	2.02	
100 0	2.63	2.00	Farkas
		(50 атм.)	Grosse
		2.58 ± 0.12	Herrick, Crist and Davis
500	1 37	—	
527	—	1.28	Crist and Dalin

TABLE 39

Comparison of Experimental and Theoretical Equilibrium Constants for the Reaction $NH_3 + HD \rightleftharpoons NH_2D + H_2$

T, °C	K_{exp}	K_{theor}	$\frac{K_{theor}}{K_{exp}}$
25	5.55	5.83	1.05
125	3.73	3.75	1.005
178.5	3.27	3.21	0.98
182.25	3 18	3.18	1 00

Fig. 17 shows the variations of the equilibrium constants of chlorine hydride and deuteride in $(-R \ln K)$ and $T^{-1} \cdot 10^3$ coordinates [54] In both cases K increases exponentially with temperature, but the slopes of the two lines differ sharply. This is to be expected, as D_2 is formed in the first instance, and HD in the second.

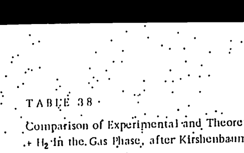


Fig 15 Comparison of calculated and theoretical values of the exchange equilibrium constants for the reaction $NH_3 + HD \rightleftharpoons NH_2D + H_2$; O) experimental, Δ) calculated.

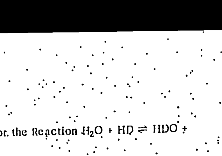


Fig. 16. Theoretically expected temperature dependence of the equilibrium constant for the reaction $H_2 + 2DI \rightleftharpoons D_2 + 2HI$, after Blagg and Murphy [53].

The above examples refer to gaseous reactions of hydrogen with large isotopic corrections, which could therefore, under otherwise equal conditions, be measured to a higher degree of accuracy. The experimental conditions conformed to the theoretical requirements. In some cases initial discrepancies between the experimental and calculated data was eliminated in subsequent work, in which sources of error were more rigorously excluded. Therefore there is no doubt about the reliability of the statistical theory of isotopic exchange constants. The observed deviations, as a rule, are caused not by defects of the theory but by inaccuracies in the experimental determinations. This is also confirmed by Table 40, in which comparative experimental and theoretical data on isotopic-exchange equilibria are summarized

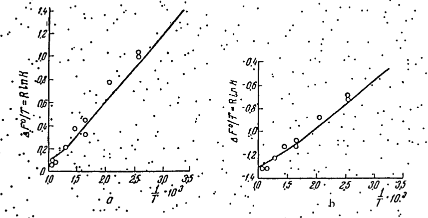


Fig. 17. Variation of equilibrium constants for the reactions: a) $H_2 + 2DCl = D_2 + 2HCl$; b) $H_2 + DCl = HD + HCl$ in $(-R \ln K)$ and $\frac{1000}{T}$ coordinates [54].

TABLE 40

Theoretical and Experimental Equilibrium Constants for Isotopic Exchange, after Zeise [48]

Reaction	T, °K	$K_{theoret}$	K_{exp}
$HD + H_2O = HOD + H_2$	800	1 36	1.28
	293	3.81	3.2
$H_2 + T_2 = 2HT$	298	2.56	2.5—2.9
$HT + H_2O = HOT + H_2$	600	1 99	2 08
	500	2 47	2 55
	400	3 46	3 52
	298.1	6.19	6 26
	273 1	7 64	7.74
$NH_3 + HD = NH_2D + H_2$	573	1.82	1.9 ± 0.1
	498	2 03	2 5
$2NH_3 + ND_3 = 3NH_2D$	298; 521	24 77	24.46
$NH_3 + 2ND_3 = 3NHD_2$	298; 521	24.22	24 08.
$PH_2D(g) + H_2O(g) = PH_3(g) + HDO(g)$	298	1 46	1 52
$H_2S + HOD = HSD + H_2O$	288	0 448.	0.453 ± 0.02
$CH_3OH + HOD = CH_3OD + H_2O$	353	0 495	0 50
	273	0.522	0 525
$n\text{-}C_5H_{11}OH + HOD = n\text{-}C_5H_{11}OD + H_2O$	298	0 49	0.50
$C_2H_5SH + HOD = C_2H_5SD + H_2O$	298	0 24	0.21

b) Exchange in heterogeneous systems

Exchange between gases and liquids

Since the final equilibrium state is independent of the route by which it is reached, in many cases unknown equilibrium constants may be calculated from known constants for other equilibria. In particular, it is possible to calculate constants for heterogeneous equilibria of isotope exchange between gases and liquids from data on homogeneous gaseous exchange equilibria and vapor pressures of isotopic substances.

In the general form, for a reaction of the type

$$\underset{\text{gas}}{AX} + \underset{\text{liquid}}{B\overset{*}{X}} \rightleftharpoons \underset{\text{gas}}{A\overset{*}{X}} + \underset{\text{liquid}}{BX}$$

the equilibrium constant $K_{g,1}$ may be found from the constant K_g for the reaction

$$\underset{\text{gas}}{AX} + \underset{\text{gas}}{B\overset{*}{X}} \rightleftharpoons \underset{\text{gas}}{A\overset{*}{X}} + \underset{\text{gas}}{BX}$$

and the equilibrium vapor pressures of the substance BX in the two isotopic forms p_{BX} and $p_{B\overset{*}{X}}$ with the aid of the obvious equation

$$K_{g,1} = K_g \frac{p_{B\overset{*}{X}}}{p_{BX}}. \tag{170}$$

In the particular case of isotopic exchange

$$\underset{\text{liquid}}{H_2O} + HD \rightleftharpoons \underset{\text{vapor}}{HDO + H_2} \rightleftharpoons \underset{\text{liquid}}{HDO} + H_2.$$

the equilibrium constant is

$$K_{g,1} = K_g \frac{p_{H_2O}}{p_{HDO}}, \tag{171}$$

where $K_g = \frac{[HDO][H_2]}{[H_2O][HD]}$. The $K_{g,1}$ constants calculated with the use of such formulas for many reactions of hydrogen and oxygen exchange of liquid water are in good agreement with the experimental values. In particular, for two reactions of hydrogen exchange with liquid water

$$\underset{\text{liquid}}{H_2O} + HD \rightleftharpoons \underset{\text{liquid}}{HDO} + H_2$$

and

$$\underset{\text{liquid}}{HDO} + D_2 \rightleftharpoons \underset{\text{liquid}}{D_2O} + HD.$$

the equation may be written

$$\left.\begin{aligned} K_1 &= K_g' \frac{p_{H_2O}}{p_{HDO}}; \\ K_2 &= K_g'' \frac{p_{HDO}}{p_{D_2O}}. \end{aligned}\right\} \tag{172}$$

K_g' and K_g'' are values of the equilibrium constant K_g, while the fractions $\frac{P_{H_2O}}{HDO}$ and $\frac{P_{HDO}}{P_{D_2O}}$ represent the ratios of the equilibrium vapor pressures of isotopic water molecules in the gas phase, from Tables 25 and 26 of §16 and Table 19 of §13.

Weston and Bigeleisen [55] made very exact determinations of the equilibrium constants for hydrogen isotope exchange between phosphine and water

$$\underset{\text{gas}}{PH_2D} + \underset{\text{liquid}}{H_2O} \rightleftharpoons \underset{\text{gas}}{PH_3} + \underset{\text{liquid}}{HDO}. \tag{173}$$

etc. As in the case of ammonia, the exchange proceeds with intermediate formation of an onium ion

$$\underset{\text{gas}}{PH_2D} + \underset{\text{liquid}}{H_2O} \rightarrow [PH_3D^+ \cdot OH^-] \rightarrow \underset{\text{gas}}{PH_3} + \underset{\text{liquid}}{HOD}, \tag{173a}$$

at T = 25°C; K = 1.63 ± 0.02.

These experimental data are used to calculate, by a method which gives no cause for doubt, the equilibrium constant for exchange in the gas phase

$$\underset{\text{gas}}{PH_2D} + \underset{\text{gas}}{H_2O} \rightleftharpoons \underset{\text{gas}}{PH_3} + \underset{\text{gas}}{HDO}, \tag{173b}$$

K_g = 1.52 at 25°C.

This value for the constant may be compared with the theoretical value with the aid of Varshavsky and Vaisberg's Table 29. From this table, at 20°C, for PH_3/H_2O α = 2.02. In the equilibrium (173b) the symmetry numbers of the PH_2D, H_2O, and PH_3 molecules differ from 1. The fraction formed by the symmetry numbers is $\frac{3}{2.2} = 3/4$. Multiplying α by this fraction, we obtain 1.51, which practically coincides with the experimental value of 1.52.

TABLE 41

Comparison of Equilibrium Constants with Calculated Values, after Zeise [illegible] and Urey [21].

Reaction	T, °K	K_{theor}	K_{exp}	Exchanged isotopes
$\frac{1}{2}C^{16}O_2 + H_2{}^{18}O_{(1)} = \frac{1}{2}C^{18}O_2 + H_2{}^{16}O_{(1)}$	273.1	1.044	1.046	$^{16}O-^{18}O$
$\frac{1}{3}C^{16}O_3{}^{2-} + H_2{}^{18}O = \frac{1}{3}C^{18}O_3{}^{2-} + H_2{}^{16}O$	273.1	1.033	1.036	$^{16}O-^{18}O$
$^{15}NH_3 + {}^{14}NH_4{}^+ = {}^{14}NH_3 + {}^{15}NH_4{}^+$	298.1	1.035	1.034	$^{15}N-^{14}N$
$HC^{14}N + C^{15}N^- = HC^{15}N + C^{14}N^-$	295	1.002	< 1	$^{14}N-^{15}N$
$^{12}CO_3{}^{2-} + {}^{13}CO_2 = {}^{13}CO_3{}^{2-} + {}^{12}CO_2$	273.1	1.016	1.017	$^{12}C-^{13}C$
$H^{12}CN + {}^{13}CN^- = H^{13}CN + {}^{12}CN^-$	295	1.030	≈1.026	$^{12}C-^{13}C$
$LiT_{(1)} + H_2 = LiH_{(1)} + H_2$	200	3.66	3.77	T − H
$^{34}SO_2 + H^{32}SO_3{}^- = {}^{32}SO_2 + H^{34}SO_3{}^-$	298.1	—	1.019	$^{32}S-^{34}S$
$^{36}SO_2 + H^{32}SO_3{}^- = {}^{32}SO_2 + H^{36}SO_3{}^-$	298.1	—	1.043	$^{32}S-^{36}S$
$^{37}ClO_4{}^- + {}^{35}ClO_2 = {}^{35}ClO_4{}^- + {}^{37}ClO_2$	298.1	—	1.052	$^{35}Cl-^{37}Cl$

The examples given above relate to hydrogen exchange equilibria.

Table 40, quoted from Zeise, gives the results of a comparison of calculated and experimental equilibrium constants for isotopic exchange equilibria of other elements. All the reactions in Table 41 represent gas−liquid exchange.

c) Experimental data on the exchange of inorganic and organic substances in solution

Fairly extensive material is available on isotopic exchange equilibria in solutions, but it has not yet been systematized. Some of it is of independent interest apart from verification of the statistical theory in view of the extensive occurrence of the reactions concerned or of their interest with regard to the theory of structure.

We now give examples of $K_{isot\,exch}$ for certain types of reactions not included in Tables 40 and 41 of §19 or of the Appendix.

Stranks and Harris [56] determined K_{equil} for isotopic exchange of C^{14} with C^{12} in a complex cobalt compound

$$[Co(NH_3)_4 \cdot C^{14}O_3^{2-}]^+ + C^{12}O_3^{2-} \rightleftarrows [Co(NH_3)_4\ C^{12}O_3^{2-}]^+ + C^{14}O_3^{2-} \qquad (174)$$

For this reaction

at 0°C $K = 0.875 \pm 0.002$;
at 30°C $K = 0.900 \pm 0.004$
and $Q_0 = \Delta E_0 = -140 \pm 25$ cal /mole.

We note the value, unusually large for carbon isotopes, of $\delta = 1 - K$.

Rutenberg and Taube [57] determined the constant for the isotopic exchange of oxygen in a complex compound of trivalent cobalt

$$[Co(NH_3)_5 \cdot H_2O^{18}]^{3+} + H_2O^{16} \rightleftarrows [Co(NH_3)_5H_2O^{16}]^{3+} + H_2O^{18} \qquad (175)$$

and found its value at 25°C to be 1.019 ±0.001. In this case the order of magnitude of $\delta = K - 1$ is normal for oxygen isotopes. A comparison of the above data with theory on the basis of model calculations and spectroscopic determinations might be of interest for the chemistry of complex compounds.

Recently hydrogen exchange of deuteroammonia and deutero acids (DBr; D_2SO_4 etc.) with hydrocarbons has attained considerable significance in relation to studies of the structure and reactivity of chemical compounds. Equilibrium constants for several examples of such exchange have been determined by A.I. Shatenshtein et al. [58]. Numerical data are given in Table 42.

TABLE 42

Equilibrium Constants for Deuterium Exchange of Hydrocarbons, after Shatenshtein et al. [58].

Hydrocarbon	Deuterium donor	K	T, °C.	Notes
Benzene C_6H_6	DF	1.1	25	(312 hr; 336 hr)
Benzene	ND_3	0.91 ± 0.02	Room	Catalyst KNH_2
Normal alkenes				
C_5H_{10}	"	0.9	20 + 50	"
C_6H_{12}	"	0.9	20 + 50	"
Cyclohexene	"	0.9	20	"
Naphthalene	"	0.9 ± 0.02	Room	"
Naphthalene	DBr	2.8	25	"

Strict theoretical calculations of equilibrium constants for hydrocarbons and deuteroammonia and deuterium bromide in the liquid phase are as yet impossible. To estimate the corrections to be introduced in the transition from gases to liquids we may compare the experimental constants in Table 42 with the calculated values for gases from Varshavsky and Vaisberg's Table 28. From this table we have $\alpha = 0.982$ for benzene with deuteroammonia. The experimental values of the constants for benzene and other aromatic compounds show greater differences from unity.

Agreement between the theory for ideal systems and the experimental data, according to Ya.M. Varshavsky, V.R. Kalinachenko and others, is better for the exchange of naphthalene with DBr:

t, °C	0	20	25	50	70
K_{exp}	3.1	3.0	2.8	2.6	2.4
K_{calc}	3.18	2.82	2.73	2.38	2.19

For alkenes, on the other hand, there is apparently a systematic qualitative discrepancy between experiment and theory. The calculated values of K vary much more than the experimental on replacement of one hydrocarbon by another.

§ 20. Summary

The data in the foregoing sections show that the statistical theory of thermodynamic isotope effects is complete with regard to homogeneous gaseous reactions, and makes it possible to calculate quantitatively the equilibrium constants from a small number of experimental spectroscopic constants. A convenient characteristic of isotopic exchange equilibria is that extremely simple rough models can be used for their calculation. This is the consequence of the almost exact agreement of most of the physical and physicochemical properties which determine the thermodynamic characteristics of a substance, in molecules differing in isotopic composition. For example, the electron levels, molecular sizes, chemical bond force constants, and, to the accuracy of the zero-point energies, the heats of dissociation are all practically identical. Dipole (and higher) electric moments; energy and form of intermolecular interaction, etc., practically coincide. Because of this, most of the thermodynamic properties in isotopic exchange are practically identical in the initial and final states of the system, and calculation of equilibrium requires only the introduction of small corrections into the simple functions of the vibrational frequencies formulated above. Hence the equations used in such calculations are simpler than the corresponding statistical theory equations for ordinary chemical equilibria. The results obtained are fully applicable to catalytic gaseous reactions, including contact processes in which solids are used as catalysts. Satisfactory results are obtained in calculations of constants for equilibria involving gases and dissolved liquids and solids. At the present time there is no theory suitable for quantitative absolute calculations of isotopic thermodynamic corrections for reactions in solutions or reactions in the solid phase.

For not especially exact calculations of constants for exchange equilibria which have not previously been investigated, the equations in § 9 will retain their importance despite the successful calculations with the use of computers. The accuracy of determination of equilibrium constants limited by difficulties in eliminating complicating side effects exceeds the accuracy of such approximate calculations only in the best investigations. In a number of cases, for purposes of orientation, it may prove convenient to use previously compiled tables using average values of fundamental frequencies of individual bonds. For the compilation of systematic tables, calculations from more exact equations with the use of electronic computers will attain primary importance. However, the accuracy attained in this way at present exceeds the accuracy of practical determinations of isotopic exchange constants. In view of the complexity of spectroscopic determinations required to obtain all the constants which appear in the more complete equations used for calculations of Z and K, and of the additional work on coding, an urgent problem is to raise the level of experimental determinations of isotopic exchange equilibrium constants. This could open a new route for investigations of the energetics and structure of molecules based on the equilibrium constants for their isotopic exchange with other molecules with well known spectroscopic constants. This applies directly to normal equilibria of stable molecules, but indirectly from measurements of the magnitudes of isotopic corrections and their dependence on external factors, it is possible to obtain interesting information on the structure and energetics of intermediate equilibrium complexes in chemical kinetics. An example of such an application of isotopic correction measurements is provided by studies on the hydration of ions based on the magnitude of isotope effects for oxygen [59]. It seems likely that with improvements of experimental methods for determination of isotopic composition this trend in the thermodynamics of isotopes will find wider applications.

LITERATURE CITED

[1] S.Z. Roginsky, D.I. Mendeleev's Periodic System of the Elements in the Light of Recent Research. Moscow, "Znanie" Press (1952).

[2] I.P. Selinov, Atomic Nuclei and Nuclear Transformations, Moscow, State Tech Press (1951)

[3] M.M. Sakharov, Dissertation, Inst. Phys. Chem., Acad. Sci USSR (1955).

[4] K. Clusius, Z. Elektrochem., 58, 586 (1954).

[5] B.B. Boltwood, Am. J. Sci. 22, 537 (1906); 24, 370 (1907); W. Marewald and B. Keetman, Ber. 41, 49 (1908); C. Auer v. Welsbach. Wien. Ber. 119, 1011 (1910).

[6] W. Marewald, Ber. 43, 3420 (1910); F. Soddy, J. Chem. Soc. 99, 72 (1911)

[7] W.M. Jones, J. Chem. Phys. 16, 1077 (1948).

[8] M.Kh. Karapetyants, Chemical Termodynamics, Moscow–Leningrad, State Chem. Press (1949); Ulich, Chemical Thermodynamics, Leningrad, State Chem. Press (1933); W. Schottky, H. Ulich and C. Wagner, Thermodynamik, Berlin, 1929.

[9] V.G. Levich, Introduction to Statistical Physics, 2nd ed., State Tech. Theoret. Press (1954); J.E. Mayer and M.G. Mayer, Statistical Mechanics, Moscow, Foreign Lit. Press (1952).

[10] V.N. Kondratyev, Structure of Atoms and Molecules, Moscow–Leningrad, Acad. Sci. USSR Press (1946).

[11] A. Farkas, Orthohydrogen, Parahydrogen, and Heavy Hydrogen, Moscow, United Sci.-Tech. Press (1936)

[12] a) G. Herzberg, Spectra and Structure of Diatomic Molecules, Moscow, Foreign Lit. Press (1949); b) G. Herzberg, Vibrational and Rotational Spectra of Polyatomic Molecules, Moscow, Foreign Lit. Press (1949).

[13] M.V. Volkenshtein, M.A. Elyashevich and B.I. Stepanov, Molecular Vibrations, Moscow–Leningrad, State Tech. Press (1949).

[14] Ya. Syrkin and M. Dyatkina, Structure of Molecules and the Chemical Bond, Moscow, State Tech. Press (1946). W. Hume-Rothery, Electrons and Metals, Moscow, Metallurgy Press (1949).

[15] L.S. Kassel, Chem. Rev. 18, 277 (1936).

[16] E. Justi, Spezifische Wärme, Enthalpie, Entropie und Dissoziation technischer Gase. Berlin, 1938.

[17] H. Zeise, Spektralphysik und Thermodynamik. Z. Elektrochem. 39, 758, 895 (1933); 40, 662, 885 (1934); 48, 425, 476, 693 (1942).

[18] A.R. Gordon, Z. Chem. Phys. 2, 65 (1934); W.F. Libby, J. Chem. Phys. 11, 101 (1943); see also [11].

[19] Gorter, Progr. Phys. Sci. 53, 545 (1954); M.A. Elyashevich, Progr. Phys. Sci. 54, 513 (1954); E. Bright and C. Wilson, Disc. Faraday Soc. No. 9, 108 (1950); A.M. Prokhorov, Nature, 44, 16 (1955).

[20] H.C. Urey and D. Rittenberg, J. Chem. Phys. 1, 137 (1933).

[21] H. Urey, Isotope Chemistry, Symposium edited by Ya.K. Syrkin, Moscow, Foreign Lit. Press (1948).

[22] J. Bigeleisen and M.G. Mayer, J. Chem. Phys. 15, 261 (1947).

[23] H.G. Trode and H.C. Urey, J. Chem. Phys. 7, 34 (1939).

[24] A.I. Brodsky, Isotope Chemistry, Moscow, Acad. Sci. USSR Press (1952).

[25] O. Redlich, Z. Phys. Chem. 28, 371 (1935); W. Angus et al., J. Chem. Soc. 971 (1936); E. Halverson, Rev. Mod. Phys. 19, 87 (1947).

[26] A.R. Striganov and Yu.P. Dontsov, Progr. Phys. Sci. 55, 315 (1955).

[27] I.M. Ryzhik, Tables of Integrals, Sums, Series, and Products, Moscow–Leningrad, State Tech. Press (1948)

[28] a) V.M. Tatevsky, J. Phys. Chem. 25, 261, 274 (1951); b) V.M. Tatevsky and A.V. Frost, Bull. Moscow State Univ. No. 12, 113 (1947).

[29] Landolt-Börnstein, B. 1, T. III. Berlin, 1951.

[30] H.C. Urey and L.J. Greiff, J. Am. Chem. Soc. 57, 321 (1935).

[31] J. Hibben, The Raman effect and its chemical applications, 1939.

[32] H. Herzberg, Astrophys. Journ. 89, 290 (1939).

[33] W.A. Chupka and M.G. Inghram, J. Chem. Phys. 21, 371, 1313 (1953); 22, 1472 (1954).

[34] R. Honig, J. Chem. Phys. 22, 126 (1954).

[35] W. Spindel, J. Chem. Phys. 22, 1271 (1954).

[36] E. Glueckauf, K.H. Barker and G.P. Kitt, Chromatographic Analysis, Disc. Far. Soc. No. 7, 199 (1949).

[37] T.I. Taylor and H.C. Urey, J. Chem. Phys. 5, 597 (1937); 6, 429 (1938).

[38] P. Harteck and R. Edse, Angew. Chem. 53, 210 (1940).

[39] G. Beggerow and P. Harteck, Z. phys. Chem. A193, 265 (1944); G. Beggerow, Dissertation, Hamburg, 1949.

[40] G. Melikonian and B. Reps, Z. Elektrochem. 58, 616 (1954)

[41] A.N. Terenin, Problems of Kinetics and Catalysis, 8, 17 (1955).

[42] S.Z. Roginsky, Adsorption and Catalysis on Heterogeneous Surfaces, Moscow, Acad. Sci. USSR Press (1948).

[43] N.P. Keier, Bull. Acad. Sci. USSR, Div. Chem. Sci. 48 (1953).

[44] I. Kirshenbaum, Heavy Water, Moscow, Foreign Lit. Press (1953).

[45] L. Landau and E. Lifshits, Statistical Physics, §92, Moscow, State Tech. Press (1951).

[46] I.B. Rabinovich, N.N. Sokolov and P.I. Artyukhin, Proc. Acad. Sci. USSR 105, 762 (1955).

[47] R. Fowler and E. Guggenheim, Statistical Thermodynamics, Moscow, Foreign Lit. Press (1949).

[48] H. Zeise, Thermodynamik, B. III/1, 1954.

[49] W.F. Gianque, J. Am. Chem. Soc. 52, 4808, 4816 (1930).

[50] Ya.M. Varshavsky and S.E. Vaisberg, J. Phys. Chem. 29, 523 (1955).

[51] a) L. Haar and A.S. Friedman, J. Chem. Phys. 22, 2051 (1954); b) ibid., 23, 869 (1955).

[52] J.F. Black and H.S. Taylor, J. Chem. Phys. 11, 395 (1943).

[53] J.C.L. Blagg and G.M. Murphy, J. Chem. Phys. 4, 631 (1936).

[54] P.C. Cross and P.A. Leighton, J. Chem. Phys. 4, 28 (1936).

[55] R. Weston and J. Bigeleisen, J. Chem. Phys. 20, 1400 (1952).

[56] D.R. Stranks and G.W. Harris, J. Phys. Chem. 56, 906 (1952).

[57] A. Rutenberg and H. Taube, J. Chem. Phys. 20, 825 (1952).

[58] Ya.M. Varshavsky and A.I. Shatenshtein, Proc. Acad. Sci. USSR 95, No. 2, 297 (1954); A.I. Shatenshtein and E.Z. Izrailevich, J. Phys. Chem. 28, No. 1,3 (1954); A.I. Shatenshtein, L.N. Vasilyeva and N.M. Dykhno, J. Phys. Chem. 28, No. 2, 193 (1954).

[59] H.M. Feder and H. Taube, J. Chem. Phys. 20, 1335 (1952); H. Taube, J. Phys. Chem. 58, 523 (1954)

CHAPTER II

KINETICS OF UNCOMPLICATED ISOTOPIC EXCHANGE

§1 Difficulties Encountered in Derivation of General Equations

The main advantage of the tagged atom method is the possibility of locating the isotope in question in systems of any degree of complexity. For this reason, the kinetics of isotopic exchange may be encountered under the most varied conditions and often in presence of complicating circumstances which greatly hinder kinetic analysis. Added to this is the diversity of mechanisms covered by the concept of isotopic exchange. Additional complications always arise if more than two substances are involved in the isotopic exchange; or if in at least one of the exchanging substances, the atoms of a particular isotope occupy different positions in the molecule, corresponding to different exchange rates.

It is therefore not surprising that special, often fairly complex mathematical investigations dealing with individual questions of the kinetics of isotopic exchange have been performed. As examples, we may cite the paper by Gest, Kamen and Reiner [1] on the use of isotopic dilution for determinations of the amounts of a substance, and the very specialized investigation of Sheppard and Hauseholder [2] of the mathematical principles of the interpretation of experiments with tagged atoms in exchange in closed flow systems. These two papers, like Solomon's paper [3] are mainly directed toward the needs of biologists, who have to apply isotope methods in especially complex conditions. The kinetics of isotopic exchange in conditions typical for chemical investigations is dealt with in publications on its individual aspects, without consideration of the problem as a whole [4, 5]. The most complete survey of work published before 1951, with an evaluation and valuable additions, is contained in the paper by Meyers and Prestwood [6]. However, both this and the other papers in this collection predominantly deal with simple cases of homogeneous exchange, proceeding by a chemical mechanism with transfer of atoms and electrons. For heterogeneous systems, only self-diffusion [7] and the nature of the participation of ions, contained within crystals of dispersed precipitates, in isotopic exchange with solutions have been studied.

The kinetics of ideal isotopic exchange was discussed in 1940 in our paper: "Kinetic Principles of the Radioactive Tracer Method" [8]. Kinetic analysis was performed only for exchange reactions between two substances, effected in static conditions.

New relationships, requiring kinetic analysis, have been revealed in experimental studies of isotopic exchange between two substances of which at least one contains several or many exchanging atoms in its molecule. The question of the kinetics of isotopic exchange involving three or more substances, and the question of the kinetics of isotopic exchange between solid surfaces and gases and solutions, in relation to heterogeneous exchange, have attained topical importance. Therefore the present monograph reviews the kinetics of isotopic exchange anew, with a summary of the older work and a detailed examination of new questions, not previously considered. It will be seen that because of the similarity of the chemical and physicochemical properties of the initial substances to those of the reaction products, it is often possible to obtain clear and simple relationships even for relatively complex cases.

§2 The Motive Force of Isotopic Exchange. True and False Equilibria

Any spontaneous process proceeds in a direction of a decrease of the free energy of the system. At constant pressure this is the Gibbs free energy or thermodynamic potential

$$\Phi = H - TS, \tag{1}$$

where H is the heat content or enthalpy of the system, T its absolute temperature, and S its entropy.

The free energy change $\Delta\Phi$ for spontaneous processes is negative

$$\Delta\Phi < 0. \tag{2}$$

This is valid, in particular, for isotopic exchange which, to an accuracy of the magnitude of the isotopic corrections considered in Chapter I, proceeds spontaneously in the direction of equipartition of the isotopes.

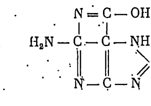
For most systems the internal energy and enthalpy, to a good degree of approximation, are independent of the distribution of the isotopes between different molecules and different phases, and also between different groups in complex molecules; at the same time, in such ideal systems isotopic exchange proceeds spontaneously. It definitely follows from this that the thermodynamic cause of isotopic exchange is the tendency of the system to decrease its free energy not by decreasing the enthalpy H, but by increasing the entropy S.

The entropy of a system is at its maximum when, with allowance for corrections introduced by differences in the amounts of different forms of energy; particles of all types are distributed according to the laws of chance, without preferential accumulation in any one part of the system. Maximum entropy corresponds to the maximum of the product TS, and hence to minimum free energy. The motive force of isotopic exchange is the increase of entropy in the redistribution of isotopes between different types of molecules, different phases, and different zones within the phases, and, finally, between different positions within the molecules. Redistribution is thermodynamically advantageous until the entropy of the system reaches its maximum value. It is only at this entropy value that the free energy Φ is at a minimum, and the system is in equilibrium with respect to isotope distribution. This question was examined in detail in our 1940 paper [8]. Using the theory of probability and the Boltzmann equation used in statistical mechanics to represent the relationship between the entropy of a system and the logarithm of its thermodynamic probability P [9, 10]

$$S = k \ln P, \tag{3}$$

we showed that for a system of any degree of complexity, consisting of n phases, each containing i molecular species including the given chemical element, the maximum entropy and equilibrium correspond to a distribution at which the relative content of any isotope is the same in any molecular form and in any phase. The derivation and the results given below are strictly applicable to ideal isotopic exchange only.* It does not matter how far the system is from ideality in its physicochemical properties.

For the components of a system which contain in their molecules atoms of a particular element in different valency states or in different structural positions, in this approximation the isotopic composition of the element should be the same in every state and position. For example, in ideal isotopic equilibrium involving 2-amino-6-hydroxypurine, i.e., guanine $C_5N_5H_5O$



guanine

which does not contain two nitrogen or carbon atoms occupying identical positions in the molecule, while there are 4 different positions for the five hydrogen atoms, there should not be any differences in the relative contents of N^{15} and N^{14} isotopes in the nitrogen atoms in the five different positions, or differences in the contents of C^{13}, C^{12}, and C^{14} in the carbon atoms in different positions, or in the deuterium and protium contents in the hydrogen in its four positions (the 2 H atoms of the amino group are regarded as chemically and structurally identical).

Carbon tetrachloride in which all the Cl^{37} isotope is present in molecules of one degree of substitution, for example in $CCl_2^{35}Cl_2^{37}$, or benzene in which, with a deuterium content other than 0 or 100%, all the deuterium is present in C_6H_5D or $C_6H_2D_4$ molecules, etc., are thermodynamically unstable. At equilibrium all the particular forms of deuterium and protium distribution in the benzene ring, for a given degree of substitution, should be present in accordance with their statistical weights. There is one such form (see later, page 100) for C_6H_5D and

---

*The meaning of these terms is discussed in Chapter 1.

C_6HD_5, and three for $C_6H_4D_2$, $C_6H_2D_4$ and $C_6H_3D_3$. In this approximation we do not consider the small differences in the isotopic composition of quinquevalent and trivalent nitrogen which remains after isotopic equilibrium has been established in nitroaniline $C_6H_4NH_2NO_2$, or in the isotopic composition of the hydrogen of the benzene nucleus and the amino group in the same compound, or, finally, between bivalent and hexavalent sulfur in the thiosulfate ion $(S=SO_3)^{2-}$. This condition of identical isotopic composition at equilibrium is applicable to different parts of a crystal or of a polycrystalline aggregate. The surface of a solid and different parts of its structure, such as edges corners, faces, intercrystalline boundaries, etc., should, in ideal systems, have the same isotopic composition as the bulk of the solid phase and the interior of each crystal.

It is proved in thermodynamics that, for ideal gases, the entropy of mixing in the transition from the limiting nonequilibrium state in which the gases are not mixed at all, to the equilibrium state, is given by Equation (4)

$$\Delta S = R\sum(-\gamma_j \cdot \ln \gamma_j), \qquad (4)$$

where γ_j is the mole fraction of the j-th gas in the mixture. Equation (4) is always positive, since $\gamma_j < 1$ and $\ln \gamma_j < 0$. As, according to the theory of equilibria, the result does not depend on the mechanism of a process, this equation may be unreservedly applied to redistribution of isotopes by means of exchange, regarding it as a special case of mixing. It can be shown that, in relation to the redistribution of isotopes, this equation is valid for systems regardless of the distance of their physicochemical properties from ideality, for example, for the equipartition of isotopes in a solid, or for concentrated solutions. The same formula determines the value of the entropy of isotope redistribution between different positions within the molecule, etc. Since the physicochemical properties of a system are not changed as the result of ideal isotopic exchange, any systems, no matter how far removed from thermodynamic ideality, behave thermodynamically as ideal gases with regard to the mixing of isotopes.

Let us consider a system of two phases, the first of which contains two molecular forms including atoms of a given element, and the second has three such forms. We denote by ρ_x the relative content of the isotope x in the whole system, by ρ_x^i its content in molecules of the i-th type, and by ${}^n\rho_x$ its content in the n-th phase. N with the corresponding subscripts represents the numbers of atoms of the corresponding isotopes x, y, and z in the system. Then

$$\rho_x = \frac{N_x}{N_x + N_y + N_z}, \qquad (5)$$

where N_x is the total number of atoms of isotope x in the system, and $N = N_x + N_y + N_z$ is the total number of atoms of the given element in the system.

Analogously, for each of the two phases we can write Equations (5a)

$$\left.\begin{aligned} {}^1\rho_x &= \frac{{}^1N_x}{{}^1N}, \\ {}^2\rho_x &= \frac{{}^2N_x}{{}^2N}, \end{aligned}\right\} \qquad (5a)$$

which give the relative contents of the isotope x in each of the phases. Finally, we denote by ρ_x'; ρ_x''; ρ_x''' etc., the relative contents of isotope x in each of the molecular forms for the whole system, and by ${}^1\rho_x'$; ${}^2\rho_x'$ etc., (5b) the contents of isotope x in the corresponding molecular form in a particular phase

$$\left.\begin{aligned} \rho_x' &= \frac{N_x'}{N'}, \\ \rho_x'' &= \frac{N_x''}{N''}, \\ {}^1\rho_x' &= \frac{{}^1N_x'}{{}^1N'}, \\ {}^2\rho_x' &= \frac{{}^2N_x'}{{}^2N'}. \end{aligned}\right\} \qquad (5b)$$

A system containing ideal isotopes is in stable equilibrium when all the separate ${}^n\rho_x^i$ are equal to each other and to ρ_x for the whole system

$$\left.\begin{aligned} {}^1\rho_x &= {}^2\rho_x = \rho_x; \\ \rho_x' &= \rho_x'' = \rho_x''' = \rho_x \\ \text{and, finally,} \quad {}^1\rho_x' &= {}^1\rho_x'' = \dots = {}^2\rho_x''' = \rho_x. \end{aligned}\right\} \qquad (6)$$

Analogous equations are valid for the contents of any other isotopes ρ_y, ρ_z of the same element and for any isotopes of other elements present in the system.

Thus, in systems containing chlorine, hydrogen, hydrogen chloride, and water, at ideal isotopic equilibrium the same definite content of Cl^{35} should be established in all phases and for all molecules; the Cl^{37} content should also be equal, though different from that of Cl^{35}; this is also true for H^1; $H^2(D)$, O^{16}; O^{17} and O^{18}, etc. Naturally, the entropy of mixing is given by the sum of the values of ΔS_j for each of the isotopes. It is easy to write similar equations for ρ and S for more complex systems, containing any number of phases, any number of molecular forms in each phase, and different positions of the isotopes within the molecules. This is the form of equipartition of isotopes to which each system tends to the accuracy of the small isotopic corrections discussed in detail in Chapter I. It must be pointed out that this limiting state may be reached at very different rates for different phases, different types of molecules, and for different structural positions of a particular isotope in the same molecule.

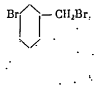
Similar effects are also possible in the simultaneous occurrence of redistribution processes for isotopes of different elements. Sharp kinetic differences frequently lead to false "retarded" equilibria in which not all the phases or all the types of molecules participate in the equipartition; or, within the molecule, only atoms of the given element linked by bonds of some definite type, present in a definite structural position, or in a definite valency state participate. For example, in the action of deuterated sulfuric acid on mixtures of saturated hydrocarbons of iso- and normal structure; according to D.N. Kursanov's data [11], equipartition of H and D between hydrocarbons of iso-structure and sulfuric acid may be expected, with the saturated hydrocarbon molecules retaining their original isotopic composition, which differs sharply from the isotopic composition of the "equalized" compounds.

We cite an example from the very interesting series of papers by A.I. Shatenshtein and his associates. Among other systems, they studied hydrogen exchange of tetralin

in solutions of deuteroammonia [12] and deuterium bromide [13]. Tetralin contains one aromatic and one methylene ring. At 20°C the rate constant for hydrogen exchange with deuteroammonia, in presence of 0.05 N potassium amide (KNH_2) as catalyst, for four hydrogen atoms of the aromatic ring has the average value $k \approx 4 \cdot 10^{-5}$ sec^{-1}. For four hydrogen atoms of the two methylene groups in the α-position relative to the aromatic ring, the rate constant is 70-100 times as great ($k \approx 10^{-3} \cdot sec^{-1}$). Finally, hydrogen from the CH_2 groups in the β-position is practically not exchanged at all. The hydrogenated tetramine ring takes practically no part in hydrogen exchange with deuterium bromide [13].

In aqueous solutions of sugars, O^{18} in heavy water is exchanged with carbonyl oxygen but not with hydroxyl oxygen, and therefore one atom out of six in glucose and fructose is exchanged.

According to our data, in isotopic exchange between inorganic bromides and organic bromides containing bromine in the aromatic nucleus and the side chain simultaneously, such as zinc bromide and dibromotoluene with the structure



containing radioactive bromine, It is easy to attain equipartition of the radioactive isotope between bromine in zinc bromide and bromine in the dibromotoluene side chain, while the bromine directly linked to the phenyl group carbon is almost unaffected [14]. If carbon dioxide and water vapor, of different oxygen isotope compositions, are passed over crystalline silica, conditions can easily be found in which the contents of O^{16}, O^{18}, and O^{17} of all the molecules present in the gas phase are equalized, While the crystalline solid retains a totally different isotopic composition. The differences are by many orders of magnitude greater than the differences caused by the small isotope effects discussed in Chapter I.

Eventually in every case true isotopic equilibrium must become established, in which all phases, all molecular forms, and all bond types of the given element present in the system participate; however, false isotopic equilibria may persist for long periods and play an important role in isotope chemistry. Retarded false equilibria cause derivations from the commonest exponential equations in isotopic exchange kinetics (see below, §3); they also make it possible to detect reactivity differences between different molecular forms and different chemical bonds, and they form the basis of the use of isotopic exchange for investigations of the chemical structure of complex molecules.

§ 3 Kinetic Types of Isotopic Exchange Reactions

a) Early studies.

Slow exchange of ions in the lattices of native minerals and crystalline precipitates obtained in the laboratory, with isotopic ions of the same elements present in aqueous solutions, was encountered even in early investigations of the chemistry of native radioactive substances [15]. Isotopic exchange proved to be one of the factors in the redistribution of radioactive substances which accompanies cocrystallization; it must also be taken into consideration in studies of the behavior of imponderable quantities of radioactive substances entrained by precipitates [16]. Paneth's well known method [15] for measurement of the surface area of precipitates by isotopic exchange is essentially based on kinetic determinations.

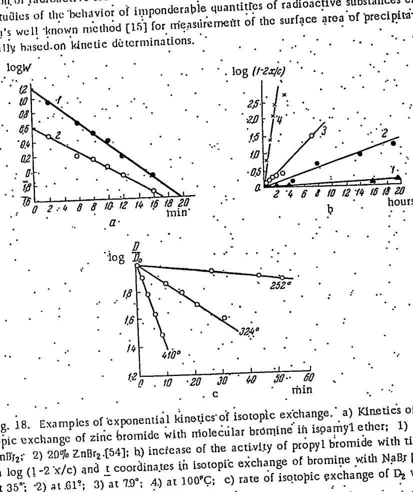


Fig. 18. Examples of exponential kinetics of isotopic exchange. a) Kinetics of isotopic exchange of zinc bromide with molecular bromine in isoamyl ether; 1) 1% $ZnBr_2$; 2) 20% $ZnBr_2$ [54]; b) increase of the activity of propyl bromide with time in log (1-2 x/c) and t coordinates in isotopic exchange of bromine with NaBr [55]; 1) at 35°; 2) at 61°; 3) at 79°; 4) at 100°C; c) rate of isotopic exchange of D_2 with H_2O in presence of platinum [52]; $\frac{D}{D_0}$ fraction of unexchanged molecules at time t.

All the above-mentioned types of isotopic exchange, however, are heterogeneous and belong to the complicated exchange category. Moreover, in these cases a number of subsidiary processes are superposed on the redistribution of radioactivity caused by isotopic exchange, and therefore special and unusual methods are required for describing their kinetics. This probably accounts for the modest nature of the contributions made by the studies of that period to an understanding of the laws of isotopic exchange kinetics. Only Doerner and Hoskins' logarithmic distribution law [17], which applies to a limiting case, is worthy of special mention.

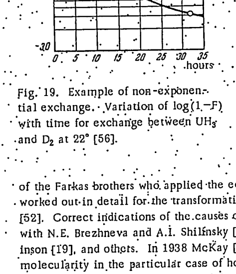


Fig. 19. Example of non-exponential exchange. Variation of log(1−F) with time for exchange between UH_3 and D_2 at 22° [56].

A very simple limiting type of isotopic exchange kinetics – a monomolecular, or, more precisely, an exponential conversion law – was met in the very first work on the applications of deuterium and artificial radioactive isotopes of ordinary elements to chemistry.

A detailed derivation and analysis of the equation for this law are given below. Its essential feature is the exponential variation with time both of the contents of the isotopes used as tagged atoms, and of the rate of approach of the system to isotopic equilibrium. To illustrate this, Fig. 18 gives three examples of reactions obeying the exponential law. In the first, for the exchange between zinc bromide and molecular bromine in benzene solution,[*] the logarithm of the velocity decreases linearly with time; in the second, which represents the specific content of radioactive bromine in propyl bromide, the value of log(1-2 x/c), increases linearly with time; and in the third, for the exchange of deuterium with water over a platinum catalyst, the logarithm of the specific content of D_2 molecules in molecular hydrogen decreases linearly. An example of sharp deviations from the exponential law, which shows that this type of exchange kinetics is widespread but not universal, is given in Fig. 19

The exponential character of exchange kinetics is found as an empirical result without a clear analysis of its origin and applicability limits in a number of investigations of the 1930's, including the work of the Farkas brothers who applied the equations and methods of determination of k and t, which they had formerly worked out in detail for the transformation of para- into ortho-hydrogen, to the isotopic exchange of deuterium [52]. Correct indications of the causes of the simplified kinetics are given in our joint experimental investigation with N.E. Brezhneva and A.I. Shilinsky [18] on the exchange of artificial radioactive isotopes, by Wilson and Dickinson [19], and others. In 1938 McKay [20] published a short theoretical note in which the transition to monomolecularity in the particular case of homogeneous bimolecular exchange $A\overset{*}{X} + BX \quad AX + B\overset{*}{X}$ was correctly assessed. However, the final result of this is not quite correct. A fuller paper by the same author was published in 1943 [21]. An expanded theoretical analysis of the origin and applicability limits of the exponential kinetics of isotopic exchange was published by us [8] in 1940. This paper also contained an explanation of and the theoretical grounds for the exponential nature of isotopic exchange catalyzed by solids, and for the retention of the exponential law for systems diverging to any extent from ideality in the physicochemical sense.

Mention must also be made of some rather later investigations, in which the same relationships were derived anew, and usually with interesting variations of the deductions and applicability Thus, Duffield and Calvin [5], in one of their investigations of the stability of chelate compounds, give a correct solution of the particular kinetic problem considered by McKay together with data on the kinetics of isotopic exchange of copper chelate compounds. Somewhat later, G. Friedlander and J. Kennedy [4] performed an analysis of the kinetics and noted the influence of some of the simplest complicating factors. An important advance is marked by the discussion of the same questions by O. Myers and R. Prestwood [6].

b) Types of isotopic exchange reactions.

Reactions in which changes of isotopic distribution occur may be divided into several groups

The first group includes processes of which the only result is a new distribution of isotopes between the different parts of the system. In such processes macroscopic changes in the system, ordinary "elementary" chemical conversions, and changes of phase composition are absent. The processes in this group cannot be detected by the

---

[*] This does not agree with the figure caption which refers to isoamyl ether rather than to benzene – Translator

ordinary chemical methods of investigation.

The second group consists of processes in which spatial displacement of a particular isotope or changes in the isotopic composition of definite phases or forms accompany ordinary physical, physicochemical, or chemical processes. In such cases observations of the displacement of a given isotope or of changes in the isotopic composition of definite forms can serve as a method for following the course of the processes, and the corresponding tagged atom or tagged molecule acts as an isotopic tracer. In practice it is often very difficult to draw a line between processes of the first group, which cover isotopic exchange reactions in the narrow sense of the word, and processes of the second group, in which isotope exchange accompanies ordinary physical, physicochemical, or chemical processes. In Chapter I processes of both groups were considered jointly. The subsequent discussion of isotopic exchange kinetics will be mainly with reference to processes of the first group.

Mention must also be made of a third, very peculiar group of processes which may lead to isotopic exchange — namely, reactions of "hot" atoms formed in nuclear reactions, including neutron capture, emission of α-particles and electrons, etc. Owing to the recoil energy, immediately after a nuclear reaction the nucleus of an atom involved in it has considerable excess energy. Under its influence, the chemical bonds by which the transmuted atom was joined to other atoms in the molecule are broken, and the bond holding the atom in its initial phase may be disturbed also. "Hot" atoms readily enter into various isotopic exchange reactions, including reactions which are difficult to bring about with ordinary "cold" atoms [22, 23].

§4 Peculiarities of Isotopic Exchange Reactions Caused by Close Similarities in the Properties of the Exchanging Atoms or Groups

Any complicated isotopic exchange reaction has certain peculiarities, common to this group of processes, regardless of its actual mechanism.

1 For the exchange of all isotopes except hydrogen, the heat effect at absolute zero (Q_0), equal to the difference between the zero-point energies of the initial and final substances, is very close to 0.

$$Q_0 = \Delta E_0 \approx 0. \tag{7}$$

For isotopic hydrogen exchange Q_0 is appreciable but small; in particular, for the reaction

$$H_2 + D_2 \rightarrow 2HD \tag{8}$$

the heat effect at T = 0 is about 160 cal/mole, or less than 1/1000 of the heat of formation of 2HD from the atoms or rather more than 1/1000 of the heat of combustion of two moles of hydrogen. Q_0 for the isotopic exchange of carbon, nitrogen, and oxygen is considerably less, and it is negligible for the isotopic exchange of such elements as phosphorus, sulfur, and chlorine.

2 With the exception of hydrogen molecules at low temperatures, the replacement of one isotope by another does not lead to any appreciable differences of heat capacity. By Kirchoff's law

$$\frac{dQ}{dT} = \sum c_{\text{init}} - \sum c_{\text{prod}} = \Delta \sum c, \tag{9}$$

where Σc_{init} is the sum of the heat capacities of the initial substances, and Σc_{prod} is the sum of the heat capacities of the reaction products.

In all cases $\Delta \Sigma c$ is very small, and it need be taken into account only in the exchange of the lightest isotopes Therefore in most cases it may be assumed with good approximation that

$$Q_T = 0. \tag{10}$$

However, even in cases in which Equation (10) cannot be used, the deviations of Q_T from 0 and the variations of the heat effects with temperature observed in practice are not large. This leads to a third, general and highly important conclusion.

3 All isotopic exchange reactions proceed with negligible heat effects, which are 2-4 orders of magnitude lower than the heat effects typical for elementary chemical reactions. In consequence, all isotopic exchange reactions occur strictly isothermally, and special heat regimes, or critical temperatures of regime changes, or thermally nonsteady states, are impossible. In fact, it can be easily shown that even one of the most exothermic isotopic exchange reactions, represented by Equation (8), when carried out adiabatically at about room temperature, can increase the temperature of the system only by 6°.

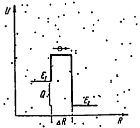


Fig. 20. Relationship between the activation energies of the forward and reverse reaction for a process with a rectangular activation barrier. The arrow represents the direction of the forward reaction; E_1 is the activation energy of the forward process; E_2 is the activation energy of the reverse process; Q is the heat of reaction; ΔR is the width of the activation barrier.

4. The heat of any reversible reaction is equal to the difference of the activation energies of the forward and reverse reactions, as shown in Fig. 20.

$$Q = E_{\text{rev}} - E_{\text{forward}} \tag{11}$$

This rule is broken only for reactions with complicated mechanisms, which proceed with large free energy changes far from equilibrium

Since, for isotopic exchange reactions, $Q \approx 0$,

$$E_{\text{rev}} \approx E_{\text{forward}} \tag{11a}$$

Deviations from this are negligible, and even for the formation of HT from $H_2 + T_2$, the heat effect of which is considerably greater than that of most other isotopic exchange reactions, Q and therefore ΔE are only 350 cal/mole. This difference is at the limit of accuracy for determinations of E by modern experimental kinetic investigation techniques.

The rule formulated above does not place any restrictions on the absolute values of E_{forward}, E_{rev} for a reaction, and it holds for any variations of the rate constant with temperature.

By the van't Hoff isochore

$$\frac{d \ln K}{dT} = \frac{Q}{RT} \tag{12}$$

Since Q = 0, the equilibrium constants should not change with temperature.

The copious numerical data in Tables 10, 23, 26, and 27 of Chapter I and in Tables 1, 2, and 3 of Section II of the Appendix show that this characteristic of ideal isotopic exchange reactions is satisfactorily obeyed. For example, for the exchange of C^{12} with C^{13} in the reaction of $C^{13}O_3^{2-}$ with $C^{12}N^-$ (see Table 10, Chapter I), K changes only from 1.126 to 1.03 as T varies from 273.1 to 600°K. The variations of K are greater for isotopic exchange involving hydrogen, but here also the dependence of K on T is at all appreciable only below 0°C. As T changes from 298.1 to 600°K (see Table 16 in the Appendix) even for $H_2 + T_2$ K changes only by a factor of 1.34 – from 2.57 to 3.45, which is approximately inversely proportional to $T^{1/2}$.

The variations of K for other reactions of this table are less. Therefore, as a rule, all cases conform satisfactorily to 4) above, with the exception of isotopic exchange involving molecular hydrogen at temperatures considerably below 0°C.

5. As is known, at equilibrium

$$K_{\text{equil}} = \frac{k_{\text{forward}}}{k_{\text{rev}}} \tag{13}$$

If the kinetic mechanism and reaction order characteristic of equilibrium are retained away from equilibrium, or if the changes in reaction orders are coordinated, Equation (13) is valid for any distance from equilibrium. At present no cases of isotopic exchange are known for which it does not hold. From Equation (13) it follows that

$$k_{\text{forward}} = K \cdot k_{\text{rev}}. \tag{13a}$$

And at the same time

$$k_{forward} = k_{\infty 1} \cdot e^{-E_1/kT};\qquad k_{rev.} = k_{\infty 2} \cdot e^{-E_2/kT}. \tag{13b}$$

From (13a) $E_2 \approx E_1$, and consequently

$$\frac{k_{\infty\,forward}}{k_{\infty\,rev}} \approx K = const. \tag{13c}$$

The ratio of the pre-exponential factors, also known as "action factors" or "kinetic frequencies," for the forward and reverse reactions is constant, and is equal to the isotopic exchange equilibrium constant. In general,

$$\frac{k_{\infty\,forward}}{k_{\infty\,rev}} = K_{\infty}, \tag{13d}$$

but for isotopic exchange usually

$$K_{\infty} \approx K. \tag{13e}$$

6 As was shown in Chapter I, above room temperatures appreciable deviations of K_{equil} from unity are possible only owing to the symmetry numbers. To a good degree of approximation (for all isotopic exchange reactions except isotopic exchange involving molecular hydrogen below 0°C).

$$K_{\infty\,equil} = \frac{\Pi\sigma_{i\,init}}{\Pi\sigma_{j\,prod}}, \tag{14}$$

where Π is the product symbol, and σ_j and σ_i are the symmetry numbers of the molecules of the reaction products and the starting substances. In the majority of cases

$$\lambda_{\sigma} = \frac{\Pi\sigma_{i\,init}}{\Pi\sigma_{j\,prod}} = 1.$$

and therefore

$$k_{\infty 1} = k_{\infty 2}. \tag{14a}$$

An exception is provided, in particular, by homomolecular reactions of the type

$$XX + \overset{*}{X}\overset{*}{X} \rightleftharpoons 2X\overset{*}{X},$$

for example, formation of HD from $D_2 + H_2$ or $Cl^{35}Cl^{37}$ from $Cl_2^{35} + Cl_2^{37}$, for which $\lambda_{\sigma} = 4$. Other types of reactions with λ_{σ}, other than unity are met, for example:

$$CH_4 + CD_4 \rightleftharpoons 2CH_2D_2,$$

or

$$CO_2^{18} + CO^{16} \rightleftharpoons CO^{18}O^{16} + CO^{18}.$$

In all such cases

$$k_{\infty 1} = k_{\infty 2} \cdot \lambda_{\sigma}. \tag{14b}$$

Conclusions (4)-(6) follow from a combination of the reversibility of isotopic exchange with far-reaching similarity between the initial substances and the reaction products. By the principle of microscopic reversibility, often also known as the detailed equilibrium principle [24], in established equilibrium every forward process passing

through definite intermediate stages should correspond to a reverse process, which passes through the same intermediate stages but in reverse sequence. If there are several forward processes, there should be the same number of reverse processes. Since the initial and final substances differ only in the isotopic compositions of the molecules, phases, or zones, all chemical reaction routes of any degree of complexity should be symmetrical to the accuracy of the isotope effect corrections and symmetry numbers

Therefore, in the approximation under consideration, for any particular mechanism of isotopic exchange all the kinetic characteristics of the forward and reverse processes should be the same. This applies to the sequence of stages, to the material transfer conditions, to the kinetic equations and activation energy equations, to the rate constants and to the action constants k_{∞} which enter into the kinetic equations of the process as a whole and of each of the parallel and consecutive reaction stages (and should apply with an accuracy to λ_{σ}) If the exchange in the forward direction proceeds by a dissociation mechanism, the mechanism should be of the same character in the reverse direction, with the same stages and the same quantitative characteristics. If the exchange proceeds by a chain mechanism, the chain carriers are analogous, and, under similar external conditions, the chains are of the same length, etc. We will illustrate this by a concrete example.

It was shown in a recent paper by Johnston and O'Shea [25] that the photochemical homomolecular isotopic exchange of oxygen $O_2^{18} + O_2^{16} \rightarrow 2O^{18}O^{16}$ occurring under irradiation by the short ultraviolet region of the quartz lamp spectrum is a chain reaction which proceeds by an atomic substitution mechanism. The chain is initiated by the photochemical generation of oxygen atoms

$$\begin{aligned} &1)\ O_2^{16} + h\nu \rightarrow O^{16} + O^{16},\\ &1')\ O_2^{18} + h\nu \rightarrow O^{18} + O^{18}, \end{aligned} \tag{15}$$

which subsequently take part in the chain reaction.

Chain propagation with the aid of the atoms proceeds according to the scheme (15a):

$$\begin{aligned} &2)\ O_2^{18} + O^{16} \rightarrow O^{16}O^{18} + O^{18},\\ &3)\ O_2^{16} + O^{18} \rightarrow O^{16}O^{18} + O^{16},\\ &2)\ O_2^{18} + O^{16} \rightarrow O^{16}O^{18} + O^{18}. \end{aligned} \tag{15a}$$

etc.

It follows that the reverse process $2O^{16}O^{18} \rightarrow O_2^{16} + O_2^{18}$ should proceed under the action of the same radiation and by a similar mechanism. Consequently the chain scheme of the reverse process will consist of the stages:

$$\begin{aligned} &4)\ O^{16} + O^{16}\cdot O^{18} \rightarrow O_2^{16} + O^{18},\\ &5)\ O^{18} + O^{16}\cdot O^{18} \rightarrow O_2^{18} + O^{16}, \end{aligned} \tag{15b}$$

etc.

The chain length ν of the forward process (15a) from the quantum yield is 125. For the reverse process ν should also be 125, etc.

8. For the more particular case of reactions obeying concentration equations, the order of the aggregate reaction is equal to the order of the forward reaction. This follows from the equality of the orders of the forward and reverse reactions. The rate is

$$w_{agg} = w_{forward} - w_{rev} = k\Pi\, c_{i\,init}^{\nu_i} - k\Pi\, c_{j\,prod}^{\nu_j}, \tag{16}$$

where $\Pi c_{i\,agg}$ is the product of the concentrations of the initial substances participating in the isotopic exchange raised to the corresponding stoichiometric powers ν_i; $\Pi c_{j\,prod}$ is the analogous product for the concentrations of the products of the exchange; k is the rate constant, common to the forward and reverse reactions Each of these products, written in expanded form, is a polynomial of the n-th order with respect to the concentration of a definite type of molecules or to the content of the isotope in molecules of a definite type, chosen as the variable

$$\Pi c^{\nu_i} = (a_1 - x)^{\nu_1} (a_2 - x)^{\nu_2} \ldots, \tag{16a}$$

where $\nu_1 + \nu_2 + \ldots = n$.

However, the difference of two polynomials of the n-th order is, in general, itself a polynomial of the same order. Therefore the order of an aggregate reversible reaction is equal to the order of the forward and reverse reactions. For odd orders this is true for the order with respect to both the initial and the current concentrations.

When $k_{forward}$ and k_{rev} are equal for even orders, the term containing x^n as factor vanishes in the subtraction $w_2 - w_1$. This diminishes by unity the order with respect to the current concentrations, while the order remains unchanged with respect to the initial concentrations. We will illustrate this with an example of an isotopic exchange reaction proceeding by a bimolecular mechanism:

$$AX + B\overset{*}{X} \rightleftharpoons A\overset{*}{X} + BX. \tag{17}$$

We denote the initial concentration AX by a and its current concentration by $(a-x)$, and the corresponding concentrations for $B\overset{*}{X}$ by b^* and (b^*-x). Suppose that at the beginning of the process $A\overset{*}{X}$ and BX are a^* and b respectively; then

$$\frac{dx}{dt} = k(a-x)(b^*-x) - k(a^*+x)(b+x) =$$

$$= k[(ab^* - a^*b) - (b + b^* + a + a^*)x] = k'(A - x), \tag{18}$$

$$k' = k(b + b^* + a + a^*) = k\sum c, \tag{18a}$$

$$A = \frac{ab^* - a^*b}{b + b^* + a + a^*}, \tag{18b}$$

where Σc is the total concentration of reacting molecules of all types, which remains constant. Equation (18) is of the first order; so that the true reaction order has decreased by unity. On the other hand, the exchange is bimolecular with respect to the relationship between w_{init} and the concentration. If we take $w_2 = 0$ and $(a-x) = a$, and, finally, $(b^*-x) = b^*$, we have

$$w_{init} = ab^*,$$

i.e., w_{init} is of the first order with respect both to a and b^*, and the total reaction order is two.

9. As is known, in chemical reaction kinetics simple concentration equations are applicable only to gases obeying the ideal gas laws, and solutions obeying the laws for ideal solutions. In the kinetics of isotopic exchange the systems most often met are far from ideality. In principle, the kinetic equations for such systems should include the activities $\bar{c}_1$, $\bar{c}_2$, etc., instead of the concentrations c_1, c_2, etc. The activities are found by multiplying the concentrations by the corresponding activity coefficients a_1, a_2, etc., which are themselves definite functions of all the concentrations c and of T.

$$\left.\begin{aligned} \bar{c}_1 &= c_1 \cdot a_1, \\ \bar{c}_2 &= c_2 \cdot a_2 \end{aligned}\right\} \tag{19}$$

etc.

A characteristic distinction of isotopic exchange reactions is that all the usual "elementary" concentrations are retained unchanged during their occurrence. Differences of isotopic composition have practically no influence on the activity coefficients, which are functions of the elementary concentrations; therefore at constant T all the functions a_1, a_2, a_3 etc., are also constant and the only variables to remain in the kinetic equations are the concentrations of forms of different isotopic compositions, or the fractional contents of these forms. There are practically no changes in the chemical or molecular composition or concentrations of any of the elementary forms. Therefore the products $\Pi a_i^{\nu_i}$ will enter the rate constant in implicit form as constant factors. As a result, simple concentration formulas are fully valid, even with very considerable deviations from the ideal gas and solution laws, in relation to the course of isotopic exchange with time [8].

This conclusion can easily be extended to the kinetic equations for catalytic isotopic exchange at solid surfaces.

10. With a completely homogeneous surface, the rate of catalytic exchange which obeys the Langmuir-Schwab equations, derived on the assumption that adsorptive equilibrium is maintained throughout the process, should be proportional to the fractions of the surface covered θ and θ_i^* raised to powers corresponding to the order of the process. Each θ_i may be regarded as the product of a certain concentration c_i and the corresponding surface activity coefficient Φ_i.

The latter are strictly constant, while the isotopic concentrations and the fractional contents of the isotopes vary during the reaction. Hence $\Pi\Phi_i^{\nu_i}$ will enter the kinetic expressions for the isotopic exchange rates in the form of constant factors implicit in the observed rate constants. The only remaining variables will be the isotope concentrations raised to the appropriate powers. In other words, the exchange will follow, instead of the Langmuir-Schwab kinetics, the concentration kinetics of homogeneous reactions applied to systems which obey the ideal gas and solution laws.

11. Catalytic processes at heterogeneous surfaces in many cases represent the sums of reactions at regions with different fractions of the surface θ_i covered by the reacting gases, but with the same form of variation of rate on θ_i in the kinetic equations. In such cases the conditions and conclusions of 10) above will be valid for isotopic exchange at each group of such regions of the surface, as in the summation of a large number of processes of the same order, the kinetic order is retained. Therefore all that was said above concerning the kinetics of catalytic isotopic exchange at homogeneous surfaces is also valid for heterogeneous surfaces.

12. As is known, the kinetic equations for catalysis at widely heterogeneous surfaces and at homogeneous surfaces coincide in presence of direct electrostatic and of more complex quasi-repulsion caused by variations of the electron-hole equilibrium [26, 27]. Hence the conclusions in 11) above are also valid for the kinetics of catalytic exchange complicated by repulsion.

13. It can be easily shown that all the foregoing is also applicable to the kinetics of isotopic exchange which proceeds in absence of a Langmuir equilibrium and which is limited by the adsorption and desorption rate in the condition that a quasi-stationary state is maintained during the reaction. It must be emphasized that isotopic exchange of adsorbed molecules with molecules in gas or liquid phases, and isotopic exchange of surface ions with dissolved ions, obey different kinetic equations, discussed in Chapter V

The relationships formulated above are strictly true only for ideal isotopic exchange reactions, in which the atoms of the exchanging isotopes are identical in chemical and physicochemical properties. For elements of moderate and high atomic weights the laws for ideal isotopic exchange reactions are in excellent approximation. For light elements, and especially for hydrogen, it is necessary in more accurate work to introduce isotopic corrections which allow for the incomplete chemical identity of the isotopes. These corrections and the differences introduced by differences of isotope weights into the absolute rates of chemical processes are considered in Chapter IV. The influence of isotopic corrections on exchange kinetics is discussed in Chapter V

The leveling of the differences of isotopic exchange kinetics in such different physicochemical conditions, noted above, is caused, in the final analysis, by the complete miscibility of isotopic molecules and the power of unlimited mutual replacement both of molecules differing only in isotopic composition, and of atoms of different isotopes. Because of this, processes in which nothing but the isotope distribution is changed occur in the thermodynamic sense both in ideal mixtures and solutions, and quasi-ideally with any phase properties. The result is a simplification of the laws for the course of isotopic exchange reactions with time, in the kinetics of which differences of phase conditions and elementary mechanisms are almost completely leveled out. This simplifies mathematical description of the course of isotopic exchange, but makes impossible direct utilization of the reaction rate isotherms for establishing the order and the stage mechanism of a process

All the factors which in the kinetics of ordinary reactions appear in w(c) are hidden in "depersonalized" rate constants. Investigations of the dependence of the latter on the elementary concentrations reveal a number of valuable quantities, including activity coefficients and adsorption isotherms. Such investigations replace studies of the course of ordinary reactions with time for elucidation of the mechanism of the process. Examples of this are shown in §8.

Having examined in detail the kinetic distinctions between isotopic exchange and ordinary chemical reactions, we will now briefly consider properties common to both processes. The dependence of the experimentally observed rate constants on temperature is such a property. In most cases the Arrhenius equation $k = k_0e^{-E/RT}$ describes the variation of the exchange rate constant with temperature highly satisfactorily. This is shown in Fig

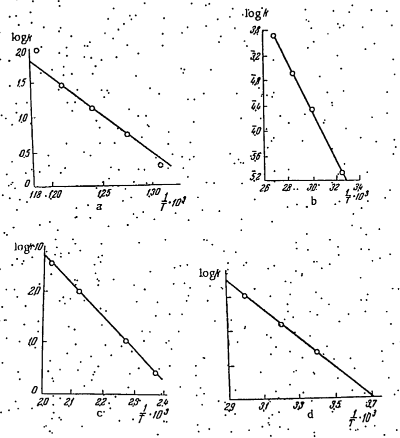


Fig 21 Temperature relationship of isotopic exchange in log k − 1/T coordinates. a) D_2 with HCl in gas phase [57]; b) C_3H_7Br with $Na\overset{*}{Br}$ [55]; c) CCl_3Br with $\overset{*}{Br}_2$ in gas phase [58]; d) $ZnBr_2$ with $\overset{*}{Br}_2$ [54].

21, in which data for two homogeneous gaseous reactions (D_2 + HCl and CCl_3Br + Br_2) and two reactions in solution (C_2H_7Br + $Na\overset{*}{Br}$ and $\overset{*}{Br}_2$ + $ZnBr_2$) are plotted in log k−1/T coordinates. In all four cases log k decreases linearly with increase of T^{-1} in accordance with the Arrhenius equation. More exact determinations sometimes reveal small deviations from linearity, which do not exceed the corrections derived from the statistical theory of activation energy with allowance for distribution of E among several degrees of freedom. In the simplest cases E_{obs} with a correction in RT or nRT is identical with E_{act} for the exchange. In more complex reactions of heterogeneous catalysis the heats of adsorption enter into the value of E_{obs}.

In was stated in §3 that exponential variation of the concentrations of isotopic molecules with time is very common in isotopic exchange. In addition to this "monomolecular" law, two other limiting types of kinetics are met: a diffusion type, in which material transfer is determining, and rapidly diminishing isotopic exchange between a phase of variable composition and a solid (see Fig. 19), an adsorbent, a surface layer of heterogeneous surface or, in homogeneous conditions, a mixture of exchanging forms with sharp differences in the exchange activation energies. There are intermediate forms between these three limiting types, and each is subdivided into several more particular kinetic groups.

We shall now derive the main types of kinetic equations for isotopic exchange with an indication of the limits and range of application. We commence with an examination of isotopic exchange kinetics in homogeneous stable systems. These may be defined as systems in which the isotopically exchanging substances are uniformly distributed in the same phase, and all the conditions with the exception of the isotope distribution between the exchanging molecules remain unchanged during the process.

§5. Simple and Complex Isotopic Exchange Reactions

a) Definition of simple and complex exchange

Irrespective of the inner mechanism, we shall term simple those isotopic exchange reactions in which only two substances are involved, each containing in its molecule one atom of the isotopically exchanged element:

$$AX + B\overset{*}{X} \longrightarrow A\overset{*}{X} + BX.$$

Complications of isotopic exchange in stable homogeneous systems may be of several types

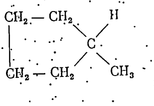
1. One or both of the exchanging molecules may contain more than one exchanging atom, present in identical conditions. For example, in the exchange of carbon tetraiodide with molecular iodine the organic molecule contains four iodine atoms identical in chemical properties, while the dissolved iodine molecule contains two such atoms:

$$\left.\begin{aligned} CI_4 + \overset{*}{I}_2 &\rightleftharpoons CI_3\overset{*}{I} + I\overset{*}{I};\\ CI_3\overset{*}{I} + \overset{*}{I}_2 &\rightleftharpoons CI_2\overset{*}{I}_2 + I\overset{*}{I};\\ CI_2\overset{*}{I}_2 + \overset{*}{I}_2 &\rightleftharpoons C I\overset{*}{I}_3 + I\overset{*}{I};\\ CI\overset{*}{I}_3 + \overset{*}{I}_2 &\rightleftharpoons C\overset{*}{I}_4 + I\overset{*}{I}. \end{aligned}\right\} \quad (20)$$

In isotopic hydrogen exchange between benzene and heavy water the benzene molecule contains six equal hydrogen atoms, and the water, two

$$C_6H_6 + D_2O \rightarrow C_6H_5D \xrightarrow{D_2O} C_6H_4D_2 \xrightarrow{D_2O} \cdots C_6D_6. \quad (21)$$

2. A very frequent kind of isotopic exchange is that in which the molecules contain atoms of the exchanging element in different positions or in different valency states, and therefore with more or less sharp differences of properties. We will add another example to those given on page 90 of this chapter. In the isotopic exchange of methylcyclopentane with deuterosulfuric acid, which has been studied in detail by D. N. Kursanov et al. [28] the hydrocarbon molecule



contains four structural types of hydrogen atoms: three primary hydrogen atoms in the methyl group, secondary hydrogen of the four methylene groups of the ring, 4 of them in the α-position and 4 in the β-position to the tertiary carbon, and finally, one hydrogen atom linked to the tertiary carbon. The number of structural forms of hydrogen is still greater in acids, alcohols, hydroxy acids, amino acids, etc. In this connection we must refer also to the example of guanine (page 87 of this chapter)

Atoms of sulfur, phosphorus, nitrogen, and other elements may be present in organic and inorganic compounds simultaneously, not only in different positions, but in different valency states, etc

3. A third type of complication occurs when more than two substances are involved in the isotopic exchange The existence of two or more phases may also serve as a source of complications. In such stable heterogeneous systems it is necessary to distinguish between complications caused by bulk differences of the phases and complications caused by special properties of the interphases

Complications of different types may be superposed, greatly hindering kinetic analysis All this applies to isotopic exchange which occurs under the influence of heat energy only, in absence of ordinary elementary reactions. However, isotopic exchange can also be induced by light, corpuscular radiation, activation by recoil energy, etc. Complicated isotopic exchange is examined in greater detail in Chapter V.

b) Homomolecular exchange system between two substances

Recently the new concept of homomolecular isotopic exchange, which includes all isotopic exchange reactions between molecules identical in chemical composition and structure but differing in isotopic composition, has appeared in the literature [25]. We have already given examples of homomolecular exchange of the simplest type for diatomic molecules of elements – hydrogen (Chapter I, §13), nitrogen and oxygen – in which only one forward reaction occurs (for example, HT + DT → HD + T_2).

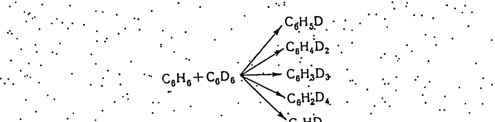
If diatomic molecules of several isotopes are involved in homomolecular exchange, or in the exchange of two isotopes in molecules consisting of more than two atoms, parallel forms of isotopic exchange appear; for example, for sulfur:

$$\left.\begin{array}{l} S^{32}\cdot\overset{*}{S}{}^{35}+S^{33}\cdot S^{34}\begin{array}{l}\nearrow S^{33}\cdot\overset{*}{S}{}^{35}+S^{32}\cdot S^{34}\\ \searrow S^{34}\cdot\overset{*}{S}{}^{35}+S^{32}\cdot S^{33}\end{array}\\ \\ S_8^{32}+S_8^{34}\begin{array}{l}\nearrow S_7^{32}\cdot S^{34}\\ \rightarrow S_5^{32}\cdot S_3^{34}\\ \searrow S_3^{32}\cdot S_5^{34}\quad \text{etc.}\end{array}\end{array}\right\}\tag{22}$$

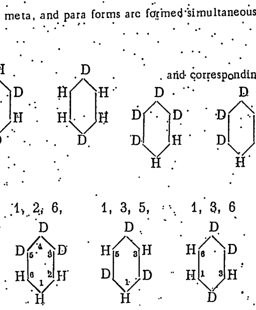
However, the main field of homomolecular exchange consists of reactions of complex molecules. Exchange in such cases may result both in changes of the number of atoms of different isotopes in a molecule, and in changes of their positions. For example, between ordinary benzene C_6H_6 and deuterobenzene C_6D_6 catalytic homomolecular exchange reactions are possible which lead to the formation of mono-, di-, tri-, tetra-, and pentadeuterobenzenes, and in the cases of the di-, tri-, and tetra-derivatives 3 forms are obtained with different relative arrangements of deuterium and protium in the molecule

$$C_6H_6+C_6D_6\begin{array}{l}\nearrow C_6H_5D\\ \nearrow C_6H_4D_2\\ \rightarrow C_6H_3D_3\\ \searrow C_6H_2D_4\\ \searrow C_6HD_5\end{array}\tag{23}$$

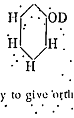
For $C_6H_4D_2$ and $C_6H_2D_4$, the ortho, meta, and para forms are formed simultaneously:



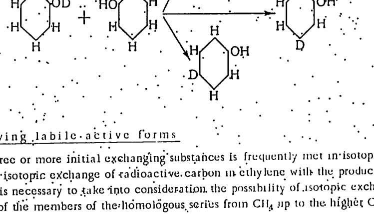
and for $C_6H_3D_3$, the forms:



Thus, hydrogen isotope exchange between molecules of ordinary benzene and hexadeuterobenzene leads to formation of 11 forms differing only in the numbers and positions of deuterium and protium atoms in the benzene molecule. Including ordinary benzene and hexadeuterobenzene, the mixture contains 13 forms capable of exchange with one another.

An interesting example of homomolecular hydrogen exchange was studied by A. I. Brodsky et al. [29] in the case of phenol. By exchange with D_2O it is easy to introduce deuterium into the hydroxyl group of phenol, to give  This reacts with ordinary phenol at elevated temperatures by a bimolecular mechanism,

probably to give ortho-, meta-, and para-deuterophenols in different proportions:*



(24)

c) Exchange involving labile-active forms

The presence of three or more initial exchanging substances is frequently met in isotopic exchange. For example, in studying the isotopic exchange of radioactive carbon in ethylene with the products of hydrocarbon synthesis for CO + H_2, it is necessary to take into consideration the possibility of isotopic exchange reactions between ethylene and any of the members of the homologous series from CH_4 up to the higher C_nH_{2n+2} hydrocarbons with n > 30. In the isotopic exchange of oxygen during catalytic oxidation of ethylene it is necessary to take into account isotopic exchange with carbon dioxide, water, ethylene oxide, etc

Even in cases in which the initial system consists of a mixture of only two individual substances in the pure state, more than two forms can actually take part in the exchange owing to the appearance of labile molecules in equilibrium with the initial molecules. Thus, in the exchange between $AlCl_3$ and organic chlorides it is necessary to take into account the presence of simple $AlCl_3$ molecules, dimeric Al_2Cl_6 molecules, and, according to some authors, also molecules of the type $HAlCl_4$; while in the exchange of ammonia and carbon dioxide with water, in addition to the original forms of NH_3, CO_2, and H_2O, allowance must be made for the formation of NH_4^+, H_3O^+, HCO_3^- and CO_3^{2-}, present in dynamic equilibrium with the initial molecules. In chain reactions, isotopic exchange occurs with radical and free atoms (for example, with CH_3, OH, CH_3COO, etc.) the concentrations of which during the reaction are far from the equilibrium values [30] Many organic reactions proceed through the agency of carbonium ions R^+, present in superequilibrium concentrations As will be shown later, nonequilibrium active forms often have increased reactivities in isotopic exchange. It is especially difficult to evaluate such exchange in the course of a reaction.

§6. The Exponential Variation of the Isotopic Concentrations of Molecules with Time

---

*The experimental procedure did not make it possible to determine their relative contents or the contents of the di-, tri-, and poly-substituted phenols which are inevitably formed.

a) Initial concepts and designations

We shall now derive the kinetic isotopic exchange equation for the simplest case of simple homogeneous ideal exchange of isotopes of an element X between compounds AX and BX, containing a tagged isotope $\overset{*}{X}$.

The isotopic exchange proceeds at a rate R, constant for a given temperature, at any distribution of X and $\overset{*}{X}$ between the two forms. Until the system, to the accuracy of the isotopic corrections, reaches equipartition with respect to $\overset{*}{X}$, this exchange leads to appreciable changes of the content of $\overset{*}{X}$ both in AX and in BX. When equipartition has become established, isotopic exchange proceeds imperceptibly at the same rate without leading to detectable results.

The following notation will be used in the derivation: t is the time; T is the temperature on the absolute scale, [A] is the total concentration of tagged and untagged X in the form of AX molecules, in gram-atoms of X per liter, [B] is the corresponding concentration of X in the form of BX molecules; R is the constant aggregate rate of exchange of atoms of X between AX and BX molecules in gram-atoms per liter per second, which is a function of the temperature, of the concentrations [A] and [B], and other factors.

$[\overset{*}{A}]$ is the concentration of the tagged isotope $\overset{*}{X}$ in AX; $[\overset{*}{B}]$ is the corresponding value for BX; ρ_A is the fractional content of isotope $\overset{*}{X}$ in AX at time t, i.e., the fraction of $\overset{*}{X}$ isotope in the atoms of X in AX; ρ_{A_0} and ρ_{A_∞} are the values for this fraction at t = 0 and t = ∞; ρ_B, ρ_{B_0} and ρ_{B_∞} are the analogous values for B; $\rho = \rho_{A_\infty} = \rho_{B_\infty}$ is the fractional content of $\overset{*}{X}$ in X at equipartition. For homogeneous systems

$$\rho_A = \frac{[\overset{*}{A}]}{[A]}; \quad \rho_B = \frac{[\overset{*}{B}]}{[B]} \tag{25}$$

etc.

F, the relative exchange, or the exchange fraction, is given by the equation

$$F = \frac{\rho_A - \rho_{A_0}}{\rho_{A_\infty} - \rho_{A_0}} = \frac{\rho_B - \rho_{B_0}}{\rho_{B_\infty} - \rho_{B_0}}. \tag{26}$$

The denominator in Equation (26) represents the difference of the fractional contents of $\overset{*}{X}$ in molecules of AX (or BX respectively) at the end of the process at equipartition, and at the beginning.

In absence of $\overset{*}{X}$ in one of the forms, for example AX, at the start of the process ($\rho_{A_0} = 0$).

$$F = \frac{\rho_A}{\rho_{A_\infty}}. \tag{26a}$$

This condition is generally fulfilled in radioactive isotope exchange.

Using Equation (25), we can rewrite (26) and (26a) as:

$$F = \frac{[\overset{*}{A}] - [\overset{*}{A}_0]}{[\overset{*}{A}_\infty] - [\overset{*}{A}_0]} = \frac{[\overset{*}{B}] - [\overset{*}{B}_0]}{[\overset{*}{B}_\infty] - [\overset{*}{B}_0]} \tag{27}$$

and

$$F = \frac{[\overset{*}{A}]}{[\overset{*}{A}_\infty]}, \tag{27a}$$

since the denominators common for all ρ_A (or all ρ_B) cancel. From (25), the fractional content of all isotopes of X except $\overset{*}{X}$ in AX and BX molecules will be

$$\left.\begin{aligned} 1 - \rho_A &= 1 - \frac{[\overset{*}{A}]}{[A]} = \frac{[A] - [\overset{*}{A}]}{[A]} \\ \text{and} \quad 1 - \rho_B &= 1 - \frac{[\overset{*}{B}]}{[B]} = \frac{[B] - [\overset{*}{B}]}{[B]}. \end{aligned}\right\} \tag{28}$$

b) Derivation of kinetic equations

With the use of this notation the equations for the kinetics of isotopic exchange can readily be derived. The rate of increase of the concentration $[\overset{*}{A}]$ with time, $\frac{d[\overset{*}{A}]}{dt} = w_{(\overset{*}{A})}$, will be the fraction α of the total rate of isotopic exchange R; this fraction varies with time and depends on how far the system is from equipartition

$$w_{(\overset{*}{A})} = \frac{d[\overset{*}{A}]}{dt} = R\alpha. \tag{29}$$

$[\overset{*}{A}]$ increases owing to the reaction between AX and $B\overset{*}{X}$ molecules and decreases owing to the reaction between $A\overset{*}{X}$ and BX molecules. The remaining processes $A\overset{*}{X}$ + AX; BX + $B\overset{*}{X}$; AX + AX; BX + BX, $A\overset{*}{X}$ + $A\overset{*}{X}$; $B\overset{*}{X}$ + $B\overset{*}{X}$ influence the value of R but do not affect α. It is clear that

$$\alpha = \alpha_1 - \alpha_2,$$

where α_1 refers to the forward and α_2 to the reverse reaction. When equilibrium is established in ideal isotopic exchange, $\alpha = 0$ and $\alpha_1 = \alpha_2$.

Since the concentrations of AX and BX molecules not containing $\overset{*}{X}$ are $[A] - [\overset{*}{A}]$ and $[B] - [\overset{*}{B}]$, and coincide with the numerators in the fractions in Equations (28) for ρ_A and $1 - \rho_B$, and since the concentrations of $A\overset{*}{X}$ and $B\overset{*}{X}$ are $[\overset{*}{A}]$ and $[\overset{*}{B}]$, from Equations (28) we obtain Equation (30).

$$\begin{aligned} \alpha_1 &= \rho_B (1 - \rho_A); \\ \alpha_2 &= \rho_A (1 - \rho_B), \end{aligned} \tag{30}$$

and hence from (29)

$$w_{(\overset{*}{A})} = \frac{d[\overset{*}{A}]}{dt} = R\rho_B (1 - \rho_A) - R\rho_A (1 - \rho_B) = R(\rho_B - \rho_A). \tag{31}$$

Equation (31) readily leads to a number of useful particular relationships. Thus, division of the left and right hand sides of the equation by [A] gives

$$\frac{d\rho_A}{dt} = \frac{R(\rho_B - \rho_A)}{[A]}. \tag{31a}$$

We now introduce $\rho \equiv \rho_{A_\infty} \equiv \rho_{B_\infty}$, the fractional content of isotope $\overset{*}{X}$ after complete equipartition has been reached (at t = ∞). If the X and $\overset{*}{X}$ nuclei are stable

$$\rho \equiv \rho_{A_\infty} \equiv \rho_{B_\infty} = \frac{[\overset{*}{A}_\infty] + [\overset{*}{B}_\infty]}{[A] + [B]} = \frac{[\overset{*}{A}] + [\overset{*}{B}]}{[A] + [B]}, \tag{32}$$

since, for stable isotopes

$$[\overset{*}{A}] + [\overset{*}{B}] = [\overset{*}{A}_\infty] + [\overset{*}{B}_\infty]. \tag{32a}$$

With radioactive isotopes a correction must be introduced for the decrease of the number of atoms with time, resulting from radioactive disintegration, which is not considered here. Finally,

$$[\overset{*}{B}_\infty] = \frac{[B]}{[A]}[\overset{*}{A}_\infty].$$

From these equations we can readily derive Equation (33)

$$\frac{d\rho_A}{dt} = \frac{[A]+[B]}{[B][A]}R(\rho - \rho_A) = r(\rho - \rho_A). \tag{33}$$

When $\rho_{A_0} = 0$, we have the equations

$$\frac{d\rho_A}{dt} = r\rho e^{-rt}. \tag{33a}$$

and

$$\rho_A = \rho(1 - e^{-rt}) \quad \text{or} \quad (\rho - \rho_A) = \rho e^{-rt} \tag{34}$$

A characteristic feature of Equations (33a) and (34) is that time enters the exponential term e^{-rt}. This term defines the exponential tendency to zero both of the rate $\frac{d\rho_A}{dt}$, and of $(\rho - \rho_A)$, which is the distance of ρ_A from the equilibrium value ρ:

In logarithmic form this equation can be written as

$$\ln\left(1 - \frac{\rho_A}{\rho}\right) = -rt. \tag{35}$$

Recently a formula identical in meaning has been more frequently used:

$$Rt = -\frac{[A][B]}{[A]+[B]} \cdot \ln(1 - F), \tag{36}$$

or

$$rt = -\ln(1-F). \tag{36a}$$

In this formula, instead of the relationship between ρ_A and ρ, the distance from isotopic equipartition is represented by the function F, which should on no account be confused with the free energy and which was defined above [see Equation (27)] as the ratio of the distance of ρ_A from the initial ρ_{A_0} to the whole range of variations of ρ_A in the transition from the initial to the equilibrium state. It must be remembered that when $\rho_{A_0} = 0$, Equation (27a) $F = \frac{\rho_A}{\rho}$ is valid. In this case the identical character of Equations (35) and (36) becomes especially evident.

It is to be noted that, from Equation (33)

$$r = R\frac{[A]+[B]}{[A][B]} = \text{const.} \tag{33b}$$

Analogs of Equation (34) are the equations

$$1 - F = e^{-rt} \tag{37}$$

and

$$F = 1 - e^{\frac{[A]+[B]}{[A][B]}Rt} = 1 - e^{-rt}. \tag{38}$$

c) Range of applicability of the derived equations

In the derivation of the final equations neither the absolute concentrations of the different isotopes, nor their ratios were limited in any way. Hence the results are valid for any absolute isotope concentrations, and not only at a low content of one of them, as was often formerly believed. It must be stressed also that conformity to the exponential law, i.e., quasi-monomolecularity in relation to time, does not require conformity to the ideal gas or solution laws, or bimolecularity of the process. The true order of an isotopic exchange reaction may have any value, integral or fractional, the system can be far from ideality, and, finally, the process may be heterogeneously catalytic, obeying laws typical for either homogeneous or heterogeneous surfaces. Exchange with a chain mechanism will obey the same exponential law. The wide though not universal applicability of Equations (33)-(38) greatly simplifies mathematical treatment of experimental results and makes such treatment uniform for very different reaction types. However, at the same time differences in the type and order of the reactions are leveled out, and the connection, usual in kinetics, between the equation describing the course of the reaction with time on the one hand, and the molarity and mechanism of the reaction on the other, is completely lost. However, this connection can be revealed by studying the influence of various factors on the experimentally observed exchange rate constants [from Equations (33)-(38)]. After r has been determined graphically or analytically, the dependence of r on the quantities in question is determined. One factor in the value of r is the fraction $\frac{[A]+[B]}{[A][B]}$, which has the dimensions of reciprocal concentration, and also R. The latter represents the total rate of exchange of atoms of X, including exchange of X with X and $\overset{*}{X}$ with $\overset{*}{X}$, i.e., the rate of exchange of atoms of element X between AX and BX at equilibrium. In general form R may be written as

$$R = kf(\bar{c}_1;\ \bar{c}_2;\ \ldots), \tag{39}$$

where $\bar{c}_i = \bar{c}_i a_i$ is the thermodynamic activity of the i-th substance, a_i is its activity coefficient, and k is the exchange rate constant.

By a comparison of systematically determined values of R, $R(c_1, c_2 \ldots)$ with formulas for simple integral powers or other equations based on definite hypotheses concerning the order and mechanism of a process, it is possible to determine the activity coefficients for homogeneous and heterogeneous reactions. From studies of the dependence of R on various quantities it is possible to establish the true order of an isotopic exchange reaction, and such studies play a prominent part in investigations of the mechanisms of these reactions.

§7. Kinetics of Isotopic Exchange in Dynamic Conditions

a) Equations for the chemical dynamics of reactions proceeding without volume change

The theoretical analysis of the kinetics of simple isotopic exchange in §6 was performed in relation to the static case. As will be shown below, closed-circulation dynamic systems are kinetically close to static systems. Nevertheless, it is often desirable to study isotopic exchange in flow systems, and there are occasions when neither static conditions nor circulation are, for various reasons, suitable. This applies primarily to the highly interesting but little studied rapid isotopic exchange reactions.

In the general case, the transition from static to dynamic conditions and back presents a complex problem for which no convenient general solutions are available. It has been shown by O. M. Todes and the author [31] that the problem is considerably simplified for reactions which proceed strictly isothermally and without change of volume. For any homogeneous reaction which satisfies these conditions the kinetic equation for static conditions can be transformed into an equation which describes the process in a flow system by substitution for the time t from the start of the reaction, of the contact time τ, which represents the average duration of displacement of the gas or liquid molecules with the stream from the point of entry into the reaction vessel to the point of observation at a distance l from the point of entry. An additional condition for the applicability of this method to contact processes is that the catalyst should retain a constant activity. The point of observation can be: the exit from the reaction vessel, the place where the catalyst layer ends, or any cross section perpendicular to the stream. For apparatus with constant cross section in parallel transfer conditions, i.e., without mixing along the flow coordinate

$$\tau = \frac{l}{u}, \tag{40}$$

where u is the linear speed of the stream.

In turn, if the apparatus through which the stream flows has constant cross section; the linear speed is

$$u = \frac{v}{s}, \tag{41}$$

where v is the space velocity and s is the area of stream cross section; hence

$$\tau = \frac{l}{u} = \frac{ls}{v} = 1. \tag{42}$$

Isotopic exchange reactions always strictly satisfy the two conditions. Their heat effects are close to zero and, as was pointed out earlier, even for the isotopic exchange reaction $H_2 + D_2 = 2HD$ the principal component of the heat of reaction, the difference of the zero-point energies, is 80 calories per mole of HD. This, on the basis of the values of the equilibrium constants and heat capacities, would, in strictly adiabatic conditions, change the temperature by less than 6°. In fact we are concerned with ΔT which is one and often 2 orders of magnitude less; therefore isotopic exchange always occurs strictly isothermally. In isotopic exchange neither the total number of molecules, nor the chemical composition of the phases, nor the intermolecular interactions within the latter are changed, therefore the volume of the system remains strictly constant. Because of the constant volume and temperature ($dv = 0$ and $\Delta T \approx 0$) the results of the investigations cited above are completely and unreservedly applicable to isotopic exchange, with the exception of a few special cases of complicated isotopic exchange, which will not be considered here. In particular, Equation (42) for transition from static to dynamic conditions is strictly applicable to isotopic exchange. This makes it possible to use the relationships between the isotopic compositions of the components and l and w for dynamic conditions, for determination of the form of the initial kinetic equation for the static case, and to calculate dynamic equations for isotopic exchange in a flow system from static conditions [32]

In view of the importance which rapid isotopic exchange reactions have recently acquired, and the associated increasing interest in isotopic exchange in flow systems, we shall present in greater detail the calculations on which Equation (42) is based.

The derivation refers to the more complex case of a heterogeneous elementary reaction in a tube filled with a solid granular catalyst (termed the charge). With this approach the equations for a homogeneous reaction in a flow system are obtained as a limiting simplified case.

The equation for the balance of the reacting substance in unit volume of the reaction vessel has the following form:

$$\frac{\partial c}{\partial t} = D_e \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} - F(c, N). \tag{43}$$

The first term in the right hand side of Equation (43) represents removal of the substance by diffusion. De is the effective diffusion coefficient in the charge in flow, which may differ considerably from the usual value of D. In a homogeneous reaction in an unpacked reaction vessel the diffusion coefficient will be different and, at sufficiently low Reynolds numbers [33] it coincides with the ordinary static coefficient of diffusion [34]. Let c be the concentration; x is the distance from the entry of the stream into the charge, which is the only coordinate in the present unidimensional problem; u is the flow rate, which in the general case is a function of x and t; $u = u(x, t)$. For a sufficiently long reaction vessel of constant cross section u is independent of x, and if the reactant is fed at a constant rate it is also independent of t. In this case, u = const. For a homogeneous system the third term F = - kf(c), where k is the rate constant; f(c) schematically represents the dependence of the reaction rates on concentration. The possibility of catalytic acceleration is allowed for by the introduction of a second variable N, i.e., by passing from f(c) to f(c, N). In the simplest case of a homogeneous catalyst surface, the rate of a catalytic reaction should be proportional to the number of active centers at a given point, and may be written as

$$F(c, N) = kNf(c) = k'f(c). \tag{44}$$

The form of the function f(c) is determined by the actual kinetics of the process. At low concentration often $f(c) = c^n$. For many reactions of single substances (n = 1), and the reaction is of the first order. In more complex cases the concentration c may enter the expression for the reaction rate raised to powers greater or lower than

unity. At high concentrations and on heterogeneous surfaces it is to be expected that f(c) will be expressed in terms of fractional concentrations or be practically independent of c, i.e., the order will be zero [27].

The proportionality factors k and k' are rate constants for the reaction. They depend on the reaction vessel temperature, and for a catalytic reaction also on the activity of the catalyst. In many cases diffusion along the flow coordinate may be neglected, assuming that

$$D_e \frac{\partial^2 c}{\partial x^2} = 0.$$

In accordance with the foregoing, for a homogeneous process Equation (43) may be transformed into (43a)

$$\frac{\partial c}{\partial t} = -u \frac{\partial c}{\partial x} - kf(c), \tag{43a}$$

and for a heterogeneous process into (43b)

$$\frac{\partial c}{dt} = -u \frac{\partial c}{\partial x} - kN(x) f(c). \tag{43b}$$

These equations must be solved for a definite distribution of the catalyst activity kN(x) along the reactor, for a given character of the f(c) function, and for definite initial and boundary conditions. For simplification of the problem it is assumed that

$$\left.\begin{aligned} &\text{at } t = 0 \quad c(x, 0) = 0, \\ &\text{at } x = 0 \quad c(0, t) = \text{const} = c_0, \end{aligned}\right\} \tag{45}$$

i.e., a gas stream with constant concentration c_0 at the entry into the charge (x = 0) enters the reaction vessel from time (t = 0).

To solve the initial equation a new variable is introduced.

$$z = \exp\left\{-\int_c^{c_0} \frac{dc}{f(c)}\right\}. \tag{46}$$

As a rule, f(c) increases steadily with c, and therefore the variable z steadily increases with c and becomes zero simultaneously with it. For reversible reactions, which include all isotopic exchange reactions, the limit at which the reaction rate becomes zero is given by the values of the concentrations representing equilibrium in the given conditions. In such cases, in the equations given, c should be taken to mean the difference between the concentrations at the given instant and at equilibrium

$$\left.\begin{aligned} &\text{at } c = 0 \quad z(0) = 0, \\ &\text{and at } c = c_0 \quad z(c_0) = 1. \end{aligned}\right\} \tag{47}$$

Substituting (46) into (43b), we obtain a linear differential equation for z in partial derivatives

$$\frac{\partial z}{\partial t} = -u \frac{\partial z}{\partial x} - a(x) z \tag{48}$$

with the following initial and boundary conditions:

$$\left.\begin{aligned} &\text{at } t = 0 \quad z(x, 0) = 0, \\ &\text{and at } x = 0 \quad z(0, t) = 1. \end{aligned}\right\} \tag{49}$$

The product of the rate constant k and the number of active centers

$$kN(x) = a(x), \tag{50}$$

we shall, for brevity, term the contact activity at a given point.

After a sufficient time interval a stationary state $\frac{\partial c}{\partial t} = \frac{\partial z}{\partial t} = 0$ is established in the reaction vessel and

$$z_{stat}(x) = \exp\left\{-\frac{1}{u}\int_0^x a(x)\,dx\right\}. \tag{51}$$

(46) and (51) may be used to find the corresponding curve for the stationary state concentration distribution in the reaction vessel, $c_{stat}(x)$ Taking further

$$z(x, t) = z_{stat}(x)\,\varphi(x, t), \tag{52}$$

we have, for the function $\varphi(x, t)$, the wave equation

$$\frac{\partial\varphi}{\partial t} = -u\frac{\partial\varphi}{\partial x}, \tag{53}$$

for a wave propagated at constant velocity equal to the gas stream velocity u.

The final solution of Equation (48), satisfying the additional conditions (49) then takes the form

$$\left.\begin{aligned} &z(x, t) = 0 \quad \text{at} \quad t < \frac{x}{u} \\ \text{and} \quad &z(x, t) = z_{stat}(x) = \exp\left\{-\frac{1}{u}\int_0^x a(x)\,dx\right\} \quad \text{at} \quad t > \frac{x}{u}. \end{aligned}\right\} \tag{54}$$

This solution corresponds to the course of the concentration curves

$$c(x, t) = 0 \text{ at } t < \frac{x}{u}$$

and

$$c(x, t) = c_{stat}(x) \text{ at } t > \frac{x}{u} \tag{55}$$

where the $c_{stat}(x)$ curve is obtained by elimination of the variable z from Equations (46) and (51) or by direct integration of the stationary state equation

$$0 = -u\frac{dc}{dx} - a(x)f(c), \tag{56}$$

obtained from Equation (43) for $\frac{\partial c}{\partial t} = 0$.

Fig. 22 shows the concentration distribution $c(x, t)$ along the reaction vessel at various consecutive times $t_1 < t_2 < t_3$ according to Equation (55).

Fig. 23 shows the corresponding course of the $c(x, t)$ concentration curves with time in several consecutive cross sections $x_1 < x_2 < x_3$ of the reaction vessel. In each section, at $t < \frac{x}{u}$, the concentration of the reacting substance $c(x, t)$ is zero. At time $t = \frac{x}{u}$ the concentration wave carried by the gas stream reaches the given point in the reactor and $c(x, t)$ instantaneously and in one step (this would be less definite on account of diffusion) reaches its final stationary value $c_{stat}(x)$. Subsequently the concentration in the given section remains unchanged, as each portion of gas reaching it passes through a layer of charge of length x in the same conditions and completely reproduces the history of the preceding portion.

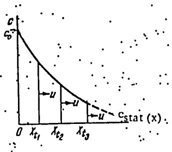


Fig. 22. Concentration distribution along the reaction vessel at times $t_1 < t_2 < t_3$ [31].

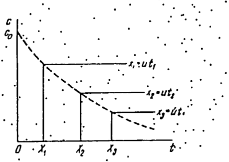


Fig. 23. Course of $c(x, t)$ concentration curves with time in several consecutive cross sections $x_1 < x_2 < x_3$ of the reaction vessel [31].

Let us consider the solution for the particular case of a first order reaction, which is of special interest in relation to isotopic exchange. For true and quasi first-order reactions, in the kinetic and also in the diffusion region*

$$f(c) = c \text{ and } z = c/c_0 \tag{57}$$

And

$$c_{stat}(x) = c_0\exp\left\{-\frac{1}{u}\int_0^x a(x)\,dx\right\} \tag{58}$$

At constant activity $a(x) = \text{const} = a$, Equation (58) becomes (58a)

$$c_{stat}(x) = c_0 e^{-\frac{a}{u}x} = c_0 e^{-a\tau}, \tag{58a}$$

i.e., the stationary state concentration along the reaction vessel diminishes purely exponentially, with the contact time τ in the exponent. The same will be found also for homogeneous reactions

The same publication [31] also contains solutions for special cases of a second order reaction, for Langmuir kinetics, etc. Subsequent papers contain derivations of dynamic equations for contact reactions on aging catalysts [35] and in presence of impurities which poison the catalyst [36]

In the original Equation (43) all the factors which depend on the temperature are collected in the last term If the function f(c) does not itself contain quantities which depend on the temperature, and if these are taken out into the factor kN = a, then only the natural scale for the length in the final expression for the stationary state concentration distribution varies with the temperature. When f(c) = c this natural scale will be given by the quantity $\xi = \frac{u}{kN}$. This is the distance over which about 2/3 of the conversion is completed (the concentration c diminishes by a factor of e).

For the general case of ideal systems the original equations contain not only the concentrations c but the activities $\bar{c}$, where $\bar{c} = ca_i$ and a_i is the activity coefficient; therefore f(c) is replaced by $f(\bar{c})$.

For heterogeneous systems in the simplest cases this leads to the inclusion in the expression kN = a, in implicit form as a multiplying factor, of one of the adsorption coefficients $b = b_0\exp\left\{\frac{Q_i}{RT}\right\}$, where Q_i is the heat of

---

*In the latter case k, and therefore a depend on u.

adsorption of the i-th component. At the same time a will nearly always contain the activation factor $e^{-E/RT}$ where E is the activation energy for the catalytic reaction.

It follows that the natural scale varies exponentially with the temperature

$$\xi = \frac{u}{kN} \sim e^{L/RT}, \tag{59}$$

where L may be equal to the activation energy (L = E), or it may be equal to the difference of the latter and the heat of adsorption (L = E − Q_{ads}) or, finally, it may include a term which depends on variation of the number of active centers N with temperature.

The value of L for contact reactions may be positive or negative. For a reaction with a positive temperature coefficient of velocity (L > 0) the natural scale diminishes with increase of temperature, while for a negative temperature coefficient the scale increases with temperature. With very rare exceptions, for homogeneous reactions in ideal systems L > 0. In non-ideal conditions L often includes heat effects of solvation processes.

The influence of temperature cannot be represented so clearly if the function f(c) itself, because of the presence of activity coefficients, contains qualities which vary sharply with temperature and which cannot be taken out as simple multiplying factors.

The equations which have been derived lead to the following simple and clear picture of a reaction in a sufficiently long reaction vessel: the reacting substance penetrates into fresh layers of the contact material at the flow rate u. As it penetrates into the charge, its concentration falls owing to chemical conversion in the preceding layers. After the stream has traveled a definite distance along the reaction vessel or through a definite thickness of the charge, a stationary distribution is established along the latter, in which the concentration of the starting substances falls in the direction of the flow. Here $\frac{\partial c}{\partial t} = 0$, and the stationary state concentration distribution is given by the equation

$$u\frac{dc}{dx} = -F(c, N), \tag{60}$$

which may be written as

$$\frac{dc}{d\left(\frac{x}{u}\right)} = \left(\frac{dc}{d\tau}\right)_{\text{reaction}} = -F(c, N). \tag{61}$$

This last equation clearly shows the complete analogy between changes of concentration with time in the kinetics of static catalytic reactions and changes of stationary state concentration with distance in dynamic conditions. The quotient of the distance from the entry and the flow rate $\frac{x}{u} = \tau$, which represents the contact time for a given portion of the starting substance, plays the same role in stationary conditions as the reaction time in the kinetics of static reactions. It may be noted that the general case of activity varying along the contact material which has been considered would correspond, in the static case, to variation of the activity of the contact material with time according to an analogous law, if only as the result of poisoning or chemical deactivation.

In static conditions, change of temperature produces an exponential variation of the time scale. In dynamic conditions, change of temperature produces an analogous variation of the spatial scale of the curves for distribution along the reaction vessel (or charge). It must be emphasized that Equation (58a), after substitution of $\frac{x}{u}$ by τ, becomes completely analogous to the first order equation written in exponential form. It is obeyed by homogeneous flow processes at $\Delta v = 0$ and $\Delta T = 0$ and contact reactions at constant catalyst activity.

b) Dynamics of isotopic exchange

The above relationships were derived for ordinary elementary chemical reactions. For reactions of isotopic

exchange all these conclusions and equations remain valid if c is replaced by $\rho - \rho_A$ or $(1 - F)$.

As was pointed out earlier, for various homogeneous and heterogeneous exchange processes between molecules containing one atom each of the given isotope (sometimes several atoms in identical positions in the molecule) of the type

$$AX + B\overset{*}{X} \rightleftharpoons A\overset{*}{X} + BX;$$

the variation of ρ_A with time can be represented by Equation (34), from which it is easy to obtain (34a)

$$\rho_A = \rho\,[1 - \exp(-rt)], \tag{34}$$

$$\rho_B = \rho\left[1 + \frac{[A]}{[B]}\exp(-rt)\right] \tag{34a}$$

where

$$\rho = \frac{\Sigma(\overset{*}{c}_i)}{\Sigma(c_i)}, \tag{62}$$

$\Sigma(\overset{*}{c}_i)$ is the total concentration of tagged molecules; $\Sigma(c_i)$ is the total concentration of all tagged and untagged molecules in the system.

For the rates of change of ρ_A and ρ_B we have

$$\frac{d\rho_A}{dt} = -\frac{[B]}{[A]}\cdot\frac{d\rho_B}{dt} = r\rho\exp(-rt), \tag{33a}$$

or, using Equation (42) to pass over to dynamic conditions, we obtain the equation

$$\rho_A = \rho\left[1 - \exp\left(-\frac{rls}{v}\right)\right]; \quad \frac{d\rho_A}{dt} = \text{const} \approx \exp\left(-\frac{rls}{v}\right). \tag{63}$$

Recently Equations (36) and (37) have been frequently used in relation to isotopic exchange. Introducing τ into these equations, we have

$$-\ln(1 - F) = \frac{(A) + (B)}{(A)(B)} Rs\,\frac{l}{v} \tag{64}$$

or

$$1 - F = e^{-\frac{rls}{v}}. \tag{65}$$

From the graphs for the variation of the logarithms of ρ_A and ρ_B or of $\ln(1 - F)$ with l and $1/v$ it is easy to find the constants r and k. The relationships of these constants with the temperature, composition of the mixture, and other parameters reveal the true kinetics of isotopic exchange, hidden in the almost universal exponential law. From Equations (63) and (64) it is also possible to determine the diffusion and intermediate conditions for heterogeneous isotopic exchange.

The above considerations show that the kinetics of isotopic exchange in dynamic conditions is no more complicated than the kinetics in static conditions, and provides the same possibilities for revealing the mechanism of the process. At the same time, for the least well studied rapid exchange reactions, the dynamic method has definite advantages over the static in certain conditions, and extends the range of systems susceptible to quantitative investigation.

Let us consider briefly the kinetics in recycling equipment. It is necessary here to distinguish between the contact time τ_c and the circulation (recycle) time τ_r. For typical cases

$$\tau_r \gg \tau_c. \tag{66}$$

The relationship between circulation kinetics and static and dynamic kinetics at low values of τ_c is determined by the character of the active species involved in the process. Let us consider the case in which these are molecules of an intermediate complex of the usual type, which exist for a very short time and are in thermodynamic equilibrium with the system. Suppose that the process occurs in dynamic conditions. Then the degree of conversion, or the degree of exchange in our particular case, is the same whether the exchanging substances are continuously present in the reaction vessel during the time $t = \tau_r$, or whether they are present in the vessel for the same time made up of any small portions Δt. For such systems which are predominant in isotopic exchange, t in the kinetic equations for static conditions may simply be replaced by $\tau_r = n\tau_c$ where τ_c is the time the substance is present in the vessel during a single pass, and n is the number of passes or cycles in time τ_r from the start of the experiment. In this case it is, of course, not permissible to use τ_c for t or to replace τ_c by the fraction ls/v.

The foregoing considerations of the relationship between recycle kinetics and the kinetics for static and dynamic conditions are also applicable to ordinary unbranched chain reactions with rapid generation of active centers and rapid succession of stages, and to autocatalytic reactions catalyzed by stable final or intermediate reaction products. The circulation technique cannot replace the static method if the reaction proceeds by way of non-equilibrium and unstable active forms, the average time of formation of which in the given reaction conditions is greater than τ_c, while their life is shorter than the time the substance is outside the reaction vessel in the course of a single cycle. In such a case there is not enough time during a single pass for a concentration of active products typical of the same process in static conditions to be established in the system; the active forms may be totally or partially destroyed while the substance is outside the reaction vessel and under different conditions, for example at another temperature or not in contact with the catalyst; therefore $t = \tau_r$ made up of n portions, each equal to τ_c, will not be kinetically equivalent to the continuous value of t. To a lesser extent these complications would also arise if the time for the formation of an active form is less than τ_c but of the same order of magnitude with it. Therefore, as a rule, before a circulation scheme is used it is necessary to verify that the continuous and discontinuous values of t are equivalent in the kinetics of the reaction to be studied, including the kinetics of isotopic exchange. Deviations from additivity can be sometimes eliminated by changes of the value of τ_c. It may be noted that circulation processes are of no value for studying rapid processes with a half-life $t_{1/2} \ll \tau_r$. A very valuable variant of the circulation technique has recently been developed by M.I. Temkin et al. [37] in the form of a flow-circulation method. It essentially consists of circulation with partial renewal of the reacting mixture. Because of this the hydromechanical conditions which determine diffusion and heat transfer correspond to the ordinary dynamic conditions and there are no changes of concentration along the length of the layer. This makes integration along the flow coordinate unnecessary, and for reactions, the rates of which are unchanged by replacement of t_{cont} by $\Sigma\Delta t_{discont}$, it becomes possible to replace t by τ.

§ 8 Determination of True Kinetic Equations and Kinetic Constants for Isotopic Exchange

1 Significance of investigations of the dependence of the kinetic exchange constants on the initial and external conditions.

Determination of the applicability of the exponential kinetic Equations (34), (36), or (64) to isotopic exchange is important for the choice of a rational method of describing the course of the process with time. However, deeper investigations of such processes do not end, but only begin here.

The exponential nature of the reaction in itself provides no indication of its mechanism, and any determination of r or R, no matter how exact, characterizes a process at only one definite chemical composition under definite external conditions.

Therefore, even in cases in which isotopic exchange is regarded as a complicating side process, and the problem is restricted to a quantitative evaluation of the exchange, it is necessary to study the influence of the initial conditions and of the state of the system on the exchange constants. It is absolutely necessary to reveal completely the often very complex functional relationships implicit in r and R for more detailed investigations the purpose of which is to determine the mechanism of isotopic exchange. This also applies to the use of isotopic exchange as a means for investigating the mechanisms of ordinary chemical reactions, or the relationships between chemical structure and reactivity. In such investigations the kinetic constants r (or R) are treated as variables. Studies of their variations with temperature, volume, nature of the solvent, the concentrations of the exchanging substances, and impurities provide valuable information on the stage mechanism and the phase conditions of a given process. Systematic determinations of this type help to determine the true kinetic characteristics of the exchange as a whole and of its individual stages. Because of the similarity of the mechanisms of isotopic exchange and of ordinary chemical reactions the results so obtained are very valuable for theoretical kinetics.

The actual methods for studying mechanisms from the exchange constants are extremely varied, they are modified in relation to the characteristics of the system in question and the nature of the problem, and therefore it is more convenient to consider some concrete examples.

2. Examples of isotopic exchange in the gas phase

a) Isotopic exchange of molecular hydrogen $H_2 + D_2 \rightleftharpoons 2HD$

An example of an isotopic exchange reaction of which the true order differs from the observed order is provided by the homomolecular isotopic exchange of hydrogen with deuterium. This reaction has been studied in the gas phase [38] and at various catalyst surfaces [39]. R Kh Burshtein [40, 41] was the first to show that this process can be effected on suitably conditioned activated sugar carbon at the temperature of liquid air. Taylor et al. [42, 43] discovered a similar low temperature reaction in presence of a number of active oxides. The usual region for catalytic exchange in presence of oxides and metals is considerably higher. The homogeneous gaseous reaction becomes appreciable above 300°C, and was studied mainly above 500°C.

In all cases and under all conditions

$$\Delta p_t^{H} = p_{H_2,t} - p_{H_2,\infty} \text{ and } \Delta p_t^{D} = p_{D_2,t} - p_{D_2,\infty}, \qquad (67)$$

which represent the differences between the partial gas pressures and the corresponding equilibrium values for a particular temperature and composition, decrease exponentially with time

$$\left.\begin{aligned} \Delta p_t^{H} &= \Delta p_0^{H} e^{-rt}, \quad \text{or} \quad [H_2]_t - [H_2]_\infty = [H_2]_0 e^{-rt}; \\ \Delta p_t^{D} &= \Delta p_0^{D} e^{-rt}, \quad \text{or} \quad [D_2]_t - [D_2]_\infty = [D_2]_0 e^{-rt}. \end{aligned}\right\} \qquad (68)$$

It is evident that these equations represent the same kinetic law as Equations (34) and (36), derived earlier in §6. The half-life, $\tau_{1/2}$ for a homogeneous reaction decreases sharply with increase of temperature, and therefore the constants $r = \frac{0.693}{\tau_{1/2}}$ increase rapidly with temperature, as shown in Fig. 24. This increase is strictly exponential. The slope of the straight line in Fig. 24 corresponds to an activation energy of 59000 cal/mole. Direct experiments with large variations of the surface area – volume ratio show the absence of any appreciable wall effects if the reactions are performed in quartz vessels. With metallic catalysts the observed activation energies are considerably less. This is clear from Table 43. To determine the true order of the process, the effect of total gas pressure on the rate constant for a monomolecular reaction, given by Equation (68), was studied. This constant proved to be proportional to the square root of the total hydrogen pressure.

$$r = r_0 [H_2]^{1/2}. \qquad (69)$$

Hence it follows that the true kinetic equation for the reaction has the form

$$w = -\frac{d(\Delta p_t^{H})}{dt} = r_0 [p_t^{H}]^{3/2}. \qquad (70)$$

The very well studied homogeneous conversion of para-hydrogen to ortho-hydrogen is of a similar order [44]. The kinetics of this reaction is so similar in all respects to the kinetics of isotope exchange [38] that it is natural to ascribe a similar mechanism to them. The value of 3/2 found for the order in both cases can be explained most simply by a reaction

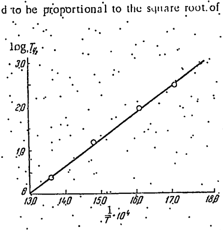


Fig. 24. Variation of the half-life ($t_{1/2}$) for the reaction $H_2 + D_2 = 2HD$ with the temperature, in log $t_{1/2}$ – T^{-1} coordinates [52].

TABLE 4.3

Activation Energies of the Heterogeneous Exchange $H_2 + D_2 \rightleftharpoons 2HD$

Catalyst	T, °C	Pressure, mm	Literature reference	E_{obs} kcal/mole
Ni, massive	14-100	0.004	Geib [39]	7.3; 10.0
C, activated	27	2.0	"	0.3*
Pt, massive	26	20.0	"	11.4
Fe, massive	20-40	20.0	"	9.0

*The small variation of the rate with temperature on active carbon may be a sign of a diffusion mechanism.

between hydrogen molecules and atoms in dynamic equilibrium with them. This equilibrium is expressed by Equations (71) and (72)

$$H_2 \rightleftharpoons 2H. \tag{71}$$

Their equilibrium constants are

$$K = \frac{p_H^2}{p_{H_2}}, \tag{72}$$

and hence

$$p_H = K^{1/2} p_{H_2}^{1/2}. \tag{73}$$

On this assumption, we have for the para–ortho conversion

$$w = \frac{d(\Delta p^{\Pi})}{dt} = k' K^{1/2} p_{H_2} p_{H_2}^{1/2} = k p_{H_2}^{3/2}. \tag{74}$$

This assumption was fully confirmed by direct determinations of the catalytic action of atomic hydrogen on the para – ortho conversion of H_2 and on the rates of exchange reactions of hydrogen atoms with molecules of different isotopic composition. On this basis we may confidently represent the isotopic exchange by the following scheme:

$$\left.\begin{aligned} &1{,}2\ a)\ H_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2H;\\ &1{,}2\ b)\ D_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2D;\\ &1{,}2\ c)\ DH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H + D;\\ &3{,}5)\quad D + H_2 \underset{k_5}{\overset{k_3}{\rightleftharpoons}} DH + H;\\ &4{,}6)\quad H + D_2 \underset{k_6}{\overset{k_4}{\rightleftharpoons}} HD + D. \end{aligned}\right\} \tag{75}$$

The consecutive occurrence of Reactions (3) and (4) leads to isotopic exchange. Dynamic equilibrium is established owing to the reverse Reactions (5) and (6).

The derivation of a relationship between the true exchange rate constant and the experimentally observed constant is difficult because of: a) the homomolecular character of the reaction, which is a complication in the kinetic sense; b) the relatively large differences between the rate constants for the exchange of H and D with different forms of molecular hydrogen; and c) differences in the dissociation constants of H_2, D_2 and HD. On equating all the values of k for the exchange and all the values of K for the dissociation, for hydrogen molecules of different isotopic composition, it can be shown that the rate constant should be given by Equation (76)

$$k = \frac{r}{K^{1/2}} \cdot f\left[(H_2)_0 + (D_2)_0\right]. \tag{76}$$

As was noted earlier, according to experimental data $r = r_0 e^{-59/RT}$, and at the same time

$$K_{H_2} = K_\infty e^{-101/RT};$$
$$K_{D_2} = K_\infty e^{-103/RT}. \tag{77}$$

Hence, since the exponent is divided by 2 when the root is taken in Equation (73), we have

$$E_{true} = 59 - \bar{Q}_{diss}/2 = 59 - 51 = 8 \text{ kcal/mole}, \tag{78}$$

where

$$\bar{Q}_{diss} = \frac{Q_{diss}^{H_2} + Q_{diss}^{D_2}}{2} \tag{79}$$

Thus, from the relationship between <u>r</u> and <u>p</u> the true order of the stage mechanism and the true energy of the given isotopic exchange reaction have been determined.

On this basis it was possible to formulate a complete quantitative theory of the homogeneous process with corrections for the tunnel effect, with calculation of the absolute rates [44], the presentation of which is outside the scope of this section.

b) Bromine and hydrogen exchange of gaseous ethyl bromide

This reaction has been studied in detail by Perry and Daniels [46], with consideration of the results of earlier investigations of the thermal decomposition of alkyl bromides [45, 46].

The process was investigated in glass vessels, at temperatures from 180 to 310°C for Br exchange and from 258 to 360°C for D exchange. In both cases the exchange obeys an exponential equation. The variation of the logarithms of 1 – F with time [see Equation (36a)] was used to determine the constants for the apparent monomolecular process

$$r = \frac{1}{t} \ln \frac{1}{1-F}. \tag{80}$$

Bromine exchange

In various experiments on bromine exchange the C_2H_5Br concentration was varied from 0.002 to 0.016 mole/liter (i.e. from 1/20 to 1/3 of an atmosphere when reduced to 0°C), and the concentration of hydrogen bromide, from $33 \cdot 10^{-6}$ to $2 \cdot 10^{-3}$ mole/liter. Assuming, for a constant rate R, certain arbitrary orders α and β with respect to ethyl bromide and hydrogen bromide

$$R = k[C_2H_5]^{\alpha}\,[HBr]^{\beta}, \tag{81}$$

the authors used Equations (33b) and (39) to write in explicit form the relationship between the true constant <u>k</u> and the apparent constant <u>r</u> for the exchange rate

$$k = r\,\frac{[C_2H_5Br]\,[HBr]}{[C_2H_5Br]^{\alpha}[HBr]^{\beta}\{[C_2H_5Br] + [HBr]\}} = r\,\frac{[C_2H_5Br]^{1-\alpha}\,[HBr]^{1-\beta}}{[C_2H_5Br] + [HBr]}. \tag{82}$$

In the main experiments, $c_{HBr} \ll c_{C_2H_5Br}$; therefore the expression for <u>k</u> may be written somewhat differently:

$$k \approx r\,[C_2H_5Br]^{-\alpha}\,[HBr]^{1-\beta}. \tag{82a}$$

In general, the values of $1-\alpha$ and $1-\beta$ may be determined by checking the constancy of r divided by different powers of $[C_2H_5Br]$ and [HBr]. For simple integral values this method is simpler than others. In the general case, it is more convenient to use log – log plots:

$$\ln r = f\left\{\ln [A]\,[B]\right\},$$

i.e., in this instance

$$\ln r = f\left\{\ln [C_2H_5Br]\,[HBr]\right\},$$

or

$$\ln \tau_{1/2} = f\{\ln [A]\};\quad \ln \tau_{1/2} = f_2\{\ln [B]\}.$$

The required exponents can be found from the slopes.

Table 44 shows the experimental results of determinations of $1-\alpha$ and $1-\beta$.

TABLE 44

Kinetics of Isotopic Exchange of C_2H_5Br with HBr, after Perry and Daniels [46]

T, °C	Time, sec · 10^3	$c_{C_2H_5Br}$ mole/liter · 10^3	$c_{H\overset{*}{B}r}$, mole/liter · 10^3	% Br* in C_2H_5Br	% Br* in HBr	r	$k=r[HBr][C_2H_5Br]^{-1}$
180	3.6	8.0	0.093	3	97	7.7×10^{-6}	5.8×10^{-8}
180	3.6	8.0	0.033	6	94	1.6×10^{-5}	6.6×10^{-8}
180	3.0	8.0	0.013	21	79	6.5×10^{-5}	1.1×10^{-7}
180	3.6	8.0	0.0033	45	55	1.6×10^{-4}	7.0×10^{-8}
200	10,8	8.0	0.28	10	90	9.6×10^{-6}	3.3×10^{-7}
200	10,8	8.0	0.28	13	87	1.4×10^{-5}	4.7×10^{-7}
200	10.8	8.0	0.28	81	19	1.7×10^{-4}	5.8×10^{-6}
200	10.8	8.0	0.28	11	89	1.2×10^{-5}	3.9×10^{-7}
200	10.8	8.0	0.28	19	81	2.0×10^{-5}	6.9×10^{-7}
254	3.6	4.6	0.23	60	40	2.8×10^{-4}	1.8×10^{-5}
254	3.6	10	0.46	60	40	2.8×10^{-4}	1.2×10^{-5}
254	3.6	4.6	0.46	39	41	1.5×10^{-4}	1.4×10^{-5}
254	3.6	2.0	0.46	19	83	6.8×10^{-5}	1.3×10^{-5}
							1.3×10^{-5}
243	1.8	16	2.0	4,5	95,5	2.9×10^{-5}	3.1×10^{-6}
243	1.8	16	1.0	9	91	5.6×10^{-5}	3.1×10^{-6}
243	1.8	16	0.40	18	82	1.1×10^{-4}	2.8×10^{-6}
243	1.8	16	0.18	36	64	2.5×10^{-4}	2.8×10^{-6}
							3.0×10^{-6}

The penultimate column gives the values of r, and the last column gives values of k found by division of r by $[C_2H_5Br]$ with constant [HBr], and by multiplication by [HBr] with constant $[C_2H_5Br]$. In view of the wide range of concentrations and the considerable variations of r, the values found for k may be regarded as proof of the validity of the equations

$$k = r[HBr]\,[C_2H_5Br]^{-1} \tag{83}$$

and

$$R = k[C_2H_5Br]\,[HBr]^0. \tag{84}$$

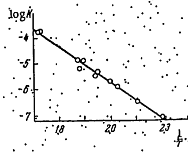


Fig. 25. Activation energy of isotopic exchange between hydrogen bromide and ethyl bromide, after Perry and Daniels [46].

It is seen that the exponential character of the influence of F in this case conceals a process with a very peculiar true order. The exponential relationship to time is well maintained, and the variation of the rate constant k with time strictly follows the Arrhenius law (Fig. 25) with an activation energy $E_{\text{isot. exch}}$ = kcal./mole.

A study of the effect of vessel dimensions on k showed that the exchange was of a heterogeneous character, commencing at the walls. The authors suggest that the bulk process proceeds by a chain mechanism, but this does not directly follow from the investigated effects of various factors on k.

Hydrogen exchange

The exchange of H of an alkyl bromide with DBr is also strictly exponential, and in the experimental conditions used by Perry and Daniels all 5 atoms of ethyl bromide participate in the exchange. Investigation of the dependence of r on the concentrations of DBr and C_2H_5Br showed that in this instance

$$r = k[C_2H_5Br]\,[HBr], \tag{85}$$

and the activation energy is approximately 40 kcal /mole, or higher than in Br exchange. Variations of the s/v ratio do not influence r, which is most simply explained by homogeneity, although the authors, without adequate basis, prefer a chain mechanism with chain initiation and termination at the walls. At present this is a controversial question, but it is undoubtedly very instructive that two different kinetic laws and two different mechanisms have been established for the exchange of H and of Br between the same molecules.

3. Exchange in solutions

Studies of the molecular mechanism of isotopic exchange based on the dependence of the observed rate constants on the concentrations of the reactants and on the external conditions have been particularly fruitful for reactions in the liquid phase. Many of the studies of isotopic exchange in solutions have dealt with charge transfer between cations, which may be schematically represented by the equation

$$Me^{\beta+} + \overset{*}{Me}{}^{\alpha+} \longrightarrow Me^{\alpha+} + \overset{*}{Me}{}^{\beta+}, \tag{86}$$

where β differs from α by one or two units.

The deep mechanism of reactions of this type is discussed in the next chapter. Here we will confine ourselves to an examination of concrete examples of methods for determination of the true order of the process from the dependence of r and R on the concentrations of the exchanging substances.

a) Isotopic exchange of the chlorides of tin

Meyer and Kahn [47] used the 27-hour radioactive isotope Sn^{121} to study the exchange of bivalent with quadrivalent tin, taken as the chlorides. The exchange was studied in absolute ethanol over the small temperature range of 25.1-42.2°C, and the total concentration of the two forms of tin was varied from 0.0438 to 0.272 mole/liter. The equation for the exchange is

$$SnCl_2 + \overset{*}{Sn}Cl_4 \rightleftharpoons \overset{*}{Sn}Cl_2 + SnCl_4. \tag{87}$$

The plot in ln(1 – F) and t coordinates shown in Fig. 26 indicates the validity of the general equation

$$-\ln(1-F) = R\,\frac{[A]+[B]}{[A]\cdot[B]}\cdot t. \tag{88}$$

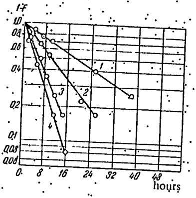


Fig. 26. Kinetics of isotopic exchange of $SnCl_2$ with $SnCl_4$ in ethanol, in 1−F and t coordinates [47], at t = 35.5°C and various concentrations:

	Sn^{2+}	Sn^{4+}	$t_{1/2}$
1 —	0.023	0.0225	10 hours
2 —	0.0416	0.0419	9.9 hours
3 —	0.0630	0.0831	5.6 hours
4 —	0.0075	0.0936	4.4 hours

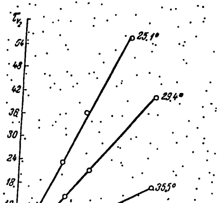


Fig. 27. Variation of $\tau_{1/2}$ with $\frac{1}{[SnCl_2] + [\overset{*}{Sn}Cl_4]}$ for the exchange of $SnCl_2$ with $\overset{*}{Sn}Cl_4$ at various temperatures [47].

TABLE 45

Exchange Kinetics of Stannous and Stannic Chlorides in Ethanol Solutions [47]

Expt. no.	T, °C	Sn^{2+} concentration, mole/liter	Sn^{4+} concentration, mole/liter	$t_{1/2}$ hours	$R \cdot 10^4$, $\frac{\text{moles}}{\text{liter} \cdot \text{hour}}$	k, $\frac{\text{moles}}{\text{liter} \cdot \text{hour}}$
1	25.1	0.0263	0.0283	57	1.66	0.222
2	25.1	0.0430	0.0460	37	4.17	0.211
3	25.1	0.0566	0.0707	24	9.53	0.217
4	29.4	0.0213	0.0225	42	1.80	0.377
5	29.4	0.0416	0.0419	22	6.57	0.377
6	29.4	0.0630	0.0629	15	14.6	0.367
7	35.5	0.0213	0.0225	19	3.99	0.833
8	35.5	0.0416	0.0419	9.9	14.4	0.838
9	35.5	0.0630	0.0831	5.6	44.4	0.847
10	35.5	0.0975	0.0936	4.4	75.3	0.825
11	42.2	0.0223	0.0411	5.6	17.9	1.95
12	42.2	0.0630	0.0629	2.9	75.1	1.90
13	42.2	0.0701	0.0381	3.4	50.4	1.89
14	42.2	0.0701	0.0381	3.4	50.4	1.89
15	42.2	0.0812	0.1913	1.3	30.3	1.95
16	42.2	0.0812	0.1913	1.3	30.3	1.95

In the present instance [A] is $[SnCl_2]$ and [B] is $[SnCl_4]$. The intersection at F = 0 of the four lines for experiments at different concentrations indicates the absence of complications, resulting from exchange, induced by precipitation and entrainment of $\overset{*}{Sn}Cl_4$ by the precipitate of stannous oxalate used for separation. When the exchange has reached half the total value, i.e., at 1−F = 0.5, from Equation (88)

$$R = \frac{[SnCl_2]\,[SnCl_4]}{[SnCl_2]+[SnCl_4]} \cdot \frac{\ln 2}{t_{1/2}}, \qquad (89)$$

where $t_{1/2}$ is the half-exchange time. In cases in which R may be written as

$$R = k[SnCl_2]^{\alpha}\,[SnCl_4]^{\beta},$$

Equation (89) becomes

$$k = \frac{[SnCl_2]^{1-\alpha}[SnCl_4]^{1-\beta}}{[SnCl_2] + [SnCl_4]} \cdot \frac{\ln 2}{t_{1/2}}, \qquad (90)$$

or

$$t_{1/2} = \frac{0{,}693\,[SnCl_2]^{1-\alpha} \cdot [SnCl_4]^{1-\beta}}{[SnCl_2] + [SnCl_4]} \cdot \frac{1}{k}. \qquad (90a)$$

When α = 1 and β = 1 the chloride concentrations vanish from the numerator of (90a):

$$t_{1/2} = \frac{0{,}693}{[SnCl_2]+[SnCl_4]} \cdot \frac{1}{k}, \qquad (91)$$

that is, at constant temperature k and, correspondingly, $t_{1/2}$ depend only on the total tin concentration in the two forms, but not on the individual concentrations. Table 45 and Fig. 27 demonstrate the good applicability of this equation. For each of the four temperatures studied, the values of k calculated from $t_{1/2}$ according to Equation (90) are constant, and the plot of $t_{1/2} = f\left(\frac{1}{[SnCl_2] + [SnCl_4]}\right)$ is strictly linear. E can be readily found from the dependence of ln k on temperature. The authors derive the following rational kinetic equation for isotopic exchange:

$$R = 5.02 \cdot 10^{16} \cdot e^{-23.7/RT}\,[SnCl_2]\,[SnCl_4], \qquad (92)$$

where R is in mole · liter^{-1} · hour^{-1}.

A bimolecular character is fairly typical of isotopic exchange of ions in solutions, but, as a rule, it is complicated by the superposition of several parallel exchange processes and various positive and negative catalytic effects. An example of this is isotopic exchange between tri- and quadrivalent cerium ions in acid solutions

b) Isotopic exchange between Ce^{3+} and Ce^{4+} in acid solutions

This reaction was studied in detail by Gryder and Dodson [18] in concentrated nitric acid and hydrochloric acid solutions. Ce^{144} with a half-life of 275 days was used as tracer. The temperature was varied from −9.8 to 25°C. Most of the experiments were carried out at 0°C.

Separation of Ce^{3+} from Ce^{4+} was effected by extraction of the latter in ethyl ether; radioactive cerium was introduced into the Ce^{4+} at a zero concentration of Ce^{144} in the Ce^{3+}. The authors were therefore able to use a simplified version of the general Equation (36):

$$\ln\left(1 - \frac{x}{x_{\infty}}\right) = -Rt(a+b)/ab = -rt, \qquad (93)$$

where x is the value of the increasing radioactivity of Ce^{3+} at time t, x_{∞} is its value at equipartition, i.e., at t = ∞; a and b have the same meaning as [A] and [B] in Equation (88), being the concentrations of the exchanging ions, a = $[Ce^{3+}]$ and b = $[Ce^{4+}]$. During any one experiment a, b, r and x_{∞} were constant while x increased from 0 to x_{∞}.

For cases in which R is a function of powers of a and b

$$R = ka^{\alpha}b^{\beta}, \qquad (94)$$

Equation (93) may be written as

$$\ln(1 - x/x_{\infty}) = -kt \cdot (a+b) \cdot a^{\alpha-1} \cdot b^{\beta-1}, \qquad (95)$$

where k is the true rate constant for the isotopic exchange. By replacing the observed rate constant by the reciprocal of the half-conversion time and taking logarithms, the following equation is obtained

$$-\ln\frac{k}{0.693} = \ln\tau_{1/2} + \ln(a+b) + (\alpha-1)\ln a + (\beta-1)\ln b. \tag{96}$$

According to this equation, ln k should be a linear function of ln a and ln b. By varying a with b constant, and b with a constant, it is easy to find the values of α and β from the slopes of the $\ln[(a+b)\tau_{1/2}] = f(\ln a)$ plots. It is evident that when the angles of inclination of the corresponding lines are φ_1 and φ_2

$$\alpha - 1 = \tan\varphi_1 \text{ or } \alpha = \tan\varphi_1 + 1 \tag{97}$$

and

$$\beta - 1 = \tan\varphi_2 \text{ or } \beta = \tan\varphi_2 + 1. \tag{97a}$$

Table 46 gives the values of $\tau_{1/2}$ for a series of experiments performed at 0°C.

TABLE 46

Exchange Kinetics of Ce Salts in Acid Solutions.

Ce^{3+} salt concentration	Ce^{4+} salt concentration	$\tau_{1/2}$, min	Ce^{3+} salt concentration	Ce^{4+} salt concentration	$\tau_{1/2}$, min.
0.00181	0 00171	88	0.00176	0.00167	94
0.00453	0 00171	45	0.00176	0.00416	61
0 00905	0.00171	25.1	0.00176	0.00831	35
0.0181	0.00171	16.7	0.00176	0.0171	20.5
0.0181	0.00171	13.3	0.00176	0.0167	23

Fig. 28 shows a log–log plot of the relationship $\tau_{1/2} = f([Ce^{3+}]/[Ce^{4+}])$ in perchlorate solution. The graph shows that the half-conversion time is practically independent of a, i.e., $\tan\varphi_1 = 0$, and consequently $\alpha = 1$. A similar situation, although not so clearly defined, was found for nitrate solutions. A similar log–log plot rises with increase of ln b on variation of the Ce^{4+} ion concentration, corresponding to $\beta \approx 0.86$. The authors take β as unity. The inhibiting action of hydrogen ions is very striking. The slope of the plot $k_{obs} = f\left\{\ln[H^+]\right\}$ indicates inverse proportionality to the square of $[H^+]$.

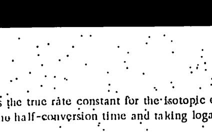


Fig. 28. Log–log plot showing the independence of the half-exchange time of Ce^{4+} with Ce^{3+}, of the Ce^{3+} concentration, after Gryder and Dodson [48].

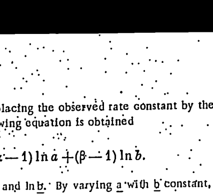


Fig. 29. Linear variation of the exchange rate constant of Ce^{4+} with Ce^{3+}, with $[H^+]^{-2}$, after Gryder and Dodson [48]

Fig. 29, plotted in the more "sensitive" coordinates k_{obs} and $\frac{1}{[H^+]^2}$, confirms this. The influence of temperature on k_{obs} was studied separately. The following final expression for the exchange rate was obtained:

$$w = \frac{dx}{dt} = [Ce^{3+}]\cdot[Ce^{4+}]\left\{2.09\cdot10^{6}\cdot e^{-7700/RT} + \frac{2.61\cdot10^{10}}{[H^+]^2}e^{-24000/RT}\right\}. \tag{98}$$

Deviations of β from 1 are ignored in this formula. The rate is given in moles per minute. This equation is equivalent to

$$w = k[Ce^{3+}][Ce^{4+}] \tag{98a}$$

with

$$k = 2.09\cdot10^{6}\exp\left(\frac{-7.7}{RT}\right) + 2.61\cdot10^{20}[H^+]^{-2}\exp\left[\frac{-24}{RT}\right]. \tag{99}$$

It is evident that the rate constant represents the sum of two constants with greatly different activation energies, of which one does not depend and the other depends strongly on $[H^+]$. According to the authors, only the first characterizes direct exchange. This work yielded an expanded quantitative equation for the exchange rate, including the order with respect to each component, the effect of H^+ ions, and a numerical expression for the rate constant by which it is possible to calculate its variation with temperature. We shall return to this paper in Chapter III when examining the deep mechanism and the stages of exchange.

c) Isotopic exchange of iodide with iodate ions

The relationships found between the observed isotopic exchange rate constants, the concentrations of the exchanging ions, and the temperature are not always so simple. The final kinetic equations frequently contain fractional powers of the exchanging ion concentrations, and more complex expressions.

Examples of such kinetics are given by O. Myers and R. Prestwood [6]. If the cause for the inapplicability of the simplest kinetic equations is variation of the thermodynamic activity coefficients or of the acidity of the solutions, the kinetic picture can often be simplified by introduction of excess electrolytes which do not participate in the exchange. Kinetic relationships remain in unusual form if the cause is complexity of stages and if intermediate forms in dynamic equilibrium with the initial and final participants in the exchange are also involved in the exchange. The existence of complications of this type has been, in particular, demonstrated with a good degree of probability in the isotopic exchange of molecular iodine with iodate ions. Practically no exchange takes place in neutral solutions. If the solution is acidified, exchange which is almost uncomplicated by elementary chemical side reactions can be induced [49]. Calculation of R from the primary kinetic data by the methods described above gives the very peculiar expression

$$R = k f_{HIO_3}^{3.6}[I_2]^{0.6}[H^+]^{1.8}[IO_3^-]^{1.8}, \tag{100}$$

where f_{HIO_3} is the activity coefficient of HIO_3.

This complex relationship is rationally explained if it is assumed that there is no direct exchange between IO_3^-, HIO_3, and I_2, but in fact I^- present in equilibrium with other iodine compounds (I_2, IO_3^-, etc.) is exchanged. Assuming a dynamic equilibrium according to the equation

$$5I^- + IO_3^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O \tag{101}$$

and expressing I_2 in terms of the equilibrium constant and the concentrations of the other components

$$[I_2] = K^{1/3}[I^-]^{5/3}[IO_3^-]^{1/3}[H^+]^2 f_{HI}^{10/3} f_{HIO_3}^{2/3}, \tag{101a}$$

it is possible to obtain from (100) a kinetic equation which corresponds, in the dependence on composition and the numerical value of k, with the direct experimental data for reaction (101) in acid solutions at low iodine concentrations [50].

d) Isotopic exchange of sulfur between disulfides and thiols in organic solvents

The observed exchange rate constants have been successfully studied in a series of investigations commenced by Ya.K. Syrkin and his associates and developed further by E.N. Guryanova and V.N. Vasilyeva [51]. They showed with the aid of radioactive sulfur S^{35} that exchange of RS groups occurs between various organic polysulfides of the type RS_nR, where n = 2, 3 etc., and polysulfides and thiols of the type RSH in organic solvents. The 1955 paper contains a detailed study of the kinetics of $\overset{*}{S}$ exchange for two systems:

1) between diparatolyl disulfide and p-thiocresol in xylene in the temperature range of 76-142°C

$$(p\text{-}CH_3C_6H_4)_2\overset{*}{S}\cdot S + p\text{-}CH_3C_6H_4SH \rightleftharpoons (p\text{-}CH_3C_6H_4)_2S_2 + p\text{-}CH_3C_6H_4\overset{*}{S}H; \qquad (102)$$

2) between dibenzyl disulfide and benzyl mercaptan in the temperature range of 180-227°C in decalin solutions

$$(C_6H_5CH_2)_2\overset{*}{S}\cdot S + C_6H_5CH_2SH \rightleftharpoons C_6H_5CH_2\overset{*}{S}H + (C_6H_5CH_2)_2S_2 \qquad (102a)$$

The course of the exchange with time and its variation with temperature are shown in Figs. 30 and 31, the first of which refers to diparatolyl disulfide, and the second to dibenzyl disulfide. In both cases, to save space, the same figure contains the variation of $\ln(1-x/x_\infty)$ with time and the variation of $\ln k_{obs}$, calculated from the slope of $\ln(1-x/x_\infty) = f(t)$ plots, with the reciprocal of the temperature.

It is clear from the figures that each of these reactions follows an exponential law in the temperature range studied. The observed scatter of the points is no more than is inevitable in studies of isotopic exchange in complex conditions. The variation of k_{obs} with temperature follows the Arrhenius law, with an activation energy of 13 kcal/mole for exchange of sulfur between ditolyl disulfide and thiocresol, and 31 kcal/mole for exchange of sulfur between dibenzyl disulfide and benzyl mercaptan.

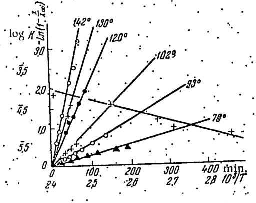


Fig. 30. Exponential character of the exchange of $CH_3C_6H_4S$ groups between diparatolyl disulfide and thiocresol, and Arrhenius type relationship between log k_{exch} and the reciprocal of the temperature [51]. x) Radioactivity of thiocresol, pulses/min at time t, x_∞) radioactivity of thiocresol at equilibrium.

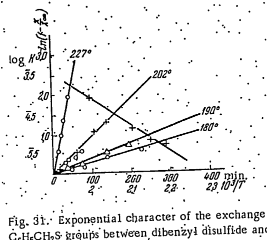


Fig. 31. Exponential character of the exchange of $C_6H_5CH_2S$ groups between dibenzyl disulfide and benzyl mercaptan in decalin, and Arrhenius type relationship between log k and 1/T [51]. x) Radioactivity of benzyl mercaptan, pulses/min at time t; x_∞) radioactivity of benzyl mercaptan at equilibrium.

Table 47, taken from the same paper, gives the results of a study of the dependence of k_{obs} on the concentrations of the components. Table 47 shows that k_{obs} is practically independent of the thiol concentration and increases with the disulfide concentration. This is clearly demonstrated by Fig. 32. The slope of the plots

$$\log k_{obs} = f(\log c_{S_2})$$

gives the following equation for the dependence of k_{obs} on c_{S_2}

$$k_{obs} = k\sqrt{c_{S_2}}, \text{ or } \quad k = \frac{k_{obs}}{\sqrt{c_{S_2}}} \qquad (103)$$

TABLE 47

Variation of k_{obs} with Component Concentration, after Guryanova and Vasilyeva

c_{SH}, mole/liter	c_{S_2}, mole/liter	$k_{obs}\cdot 10^3$, min^{-1}	$k = \frac{k_{obs}}{\sqrt{c_{S_2}}}$	Note
Dipatatolyl disulfide – thiocresol, 120°C				
0.05	0.1	0.45	1.4	For brevity, here and subsequently c_{RSH} is replaced by c_{SH} and $c_{R_2S_2} - c_{S_2}$
0.1	0.1	0.38	1.2	
0.3	0.1	0.40	1.3	
0.1	0.05	0.26	1.2	
0.1	0.1	0.38	1.2	
0.1	0.5	0.93	1.3	
Dibenzyl disulfide – benzyl mercaptan, 202°C				
0.25	0.5	0.10	0.14	
0.50	0.5	0.13	0.18	
1.0	0.5	0.11	0.16	
2.5	0.5	0.11	0.16	
0.5	0.5	0.13	0.18	
0.5	1.0	0.17	0.17	
0.5	2.5	0.32	0.20	

The constants calculated from this equation are given in the fourth column of Table 47. As was shown in the discussion of the preceding examples, the exponents of the concentrations of the exchanging substances in the expression for k_{obs} correspond to the true orders of α and β, diminished by 1. Therefore from Guryanova and Vasilyeva's data,

$$\left.\begin{aligned} &\alpha - 1 = 0 \text{ or } \alpha = 1 \\ \text{and} \quad &\beta - 1 = {}^1/_2 \text{ or } \beta = {}^3/_2 \end{aligned}\right\} \qquad (104)$$

and the equation for the rate is

$$w = kc_{SH}\,c_{S_2}^{1/2}. \qquad (105)$$

These are the valuable actual results of this carefully performed investigation. The conclusions reached by the authors with regard to the kinetics differ from ours, as they used a different method for calculation of the true orders of reaction. With the almost constant values of k in Table 47, calculated from Equation (103) as basis, the authors, apparently ignoring Equations (104), identified the observed and the true relationships between k_{obs} and c_{SH} and c_{S_2}; i.e., they neglected the factor $\frac{1}{[A]\cdot[B]}$ in the original kinetic equation. From this, 1) it is concluded that the dissociation products $R\overset{*}{S}$ of the disulfide participate in the reaction, and 2) decomposition into radicals according to the equation

$$R\overset{*}{S} - SR \rightleftharpoons R\overset{*}{S} + RS \qquad (106)$$

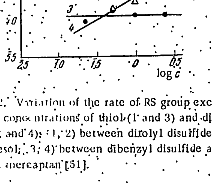


Fig. 32. Variation of the rate of RS group exchange on the concentrations of thiol (1 and 3) and disulfide (2 and 4): 1, 2) between ditolyl disulfide and thiocresol; 3, 4) between dibenzyl disulfide and benzyl mercaptan [51].

is taken as the rate determining stage. We cannot agree with this. The rate of the determining stage, according to the experimental data of Guryanova and Vasilyeva, is proportional to $c_{S_2}^{3/2} c_{SH}$ while for Reaction (106) the second factor is absent. We may note here that in general the determining role of dissociation into radicals does not follow from $w \sim \sqrt{c_{S_2}}$.

4. Heterogeneous catalytic exchange

The methods which have been given for determination of true reaction orders from the variations of the observed isotopic exchange rate constants are fully applicable to heterogeneous catalytic exchange. Heterogeneous exchange of hydrogen can serve as an example. There have been very many investigations of the kinetics of catalytic exchange of gaseous deuterium with protium and various inorganic and organic substances. Many of these investigations were made on substances containing several or many hydrogen atoms in their molecules (NH_3, CH_4, C_2H_6, C_4H_{10} etc.) without allowance for the complications caused by participation of molecules of different degrees of substitution in the exchange (see Chapter V). The class of simple exchange reactions includes only reactions of the type HX + DY, such as HI + DBr or $CHCl_3$ + DF; however, catalytic exchange in reactions of this type has not been sufficiently studied, and therefore we shall only use data on the exchange of H_2 with D_2 and D_2 with C_2H_5OH. In the latter case it has been shown by careful control experiments that of the six hydrogen atoms only the hydroxyl hydrogen participates in isotopic exchange. The most systematic studies were those made by the Farkas brothers, Polanyi, and Horiuti, who mainly used platinum in various forms as catalyst [38, 52, 53]. The exchange follows an exponential law. If the molecular hydrogen was initially artificially enriched with deuterium, the course of the exchange is represented by the equation

$$D_t = D_0 e^{-kt}, \qquad (107)$$

where D_t is ρ_D for molecular hydrogen at time t; and D_0 is the corresponding value at the start.

In logarithmic form Equation (107) corresponds to

$$\ln = \frac{D_t}{D_0} = -kt. \qquad (108)$$

This is one of the simplified forms of the general Equation (34). Good agreement with Equation (108) is so systematic that deviations from linearity served as definite indications of catalyst poisoning during the process, while their magnitude could serve as a satisfactory measure of loss of catalyst activity. This method was used with great success by R. Kh. Burshtein in her investigations of isotopic exchange between D_2 and H_2 on active carbon [40, 41] at temperatures from −190°C. By comparing the rate constants of monomolecular exchange for different specimens of carbon, the surfaces of which had been previously covered at 500°C with exactly measured amounts of activation-adsorbed hydrogen, R. Kh. Burshtein was able to determine accurately the total number of active centers per unit surface of active carbons of various origins. She showed that the active centers cannot contain the ash elements, and obtained statistical data on the activity of these centers. A graph to illustrate this is shown in Fig. 33.

This graph shows that the rate constant, expressed as $\frac{1}{\tau_{1/2}} \cdot 10^4$, falls linearly to zero when only 0.01% of the surface is covered. The linear decrease of k_{obs} indicates that there are no appreciable differences of activity between different regions in this group. At the same time, experiments on the para−ortho conversion and chemisorption of hydrogen on the same carbon show that there are 30 times as many regions which are capable of bringing about the p → o conversion but do not catalyze the formation of HD from D_2 and H_2. There are also

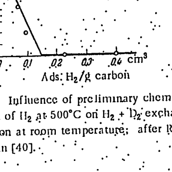


Fig. 33: Influence of preliminary chemisorption of H_2 at 500°C on H_2 + D_2 exchange on carbon at room temperature; after R. Kh. Burshtein [40].

regions which do not catalyze either of these reactions under these conditions. This example shows that it is possible to study the properties of active surfaces from the influence of catalyst poisons on k_{obs} for catalytic exchange. The true order of an exchange reaction can be investigated in the same way. Unfortunately, it is very rarely found to be constant, as the rate equations contain the surface concentrations, which are only linearly related to the volume concentrations at low degrees of surface covering. This complicates the application of this method to heterogeneous exchange, as extensive data are required. Nevertheless, the dependence of r on [A] and [B] in catalytic exchange has rarely been studied. In particular, it was not studied in Burshtein's investigation

Let us now return to the results obtained by Farkas. The experimental rate constants for the exchange of ethanol with deuterium were found to depend little on the partial hydrogen pressure. As is seen from the small Table 48, which refers to room temperature, the half-conversion time is increased approximately 1.5 times for a 10-fold increase of $[H_2]$. Consequently, k_{obs} decreases. This corresponds to $k_{obs} \sim$ $\sim [H_2]^{\alpha}$ where α is somewhat less than 1 (of the order of 0.9). The variation of k_{obs} with partial pressure of ethanol vapor, varied over a 12000-fold range, is shown in Fig. 34 as a bilogarithmic plot $\log \tau_{1/2} = f(\log p_{alc})$. Over a fairly wide range of p (0.3-28), $\tau_{1/2}$ is practically constant. This corresponds to a first order reaction, $\beta \approx 1$. At low values of p_{alc}, $\tau_{1/2}$ decreases rather more rapidly than $\sqrt{p_{alc}}$, while R increases. This gives $\alpha \approx$ ≈ 1.5. A more detailed investigation reveals a very flat maximum for R at a definite ratio of p_{H_2} to p_{alc}.

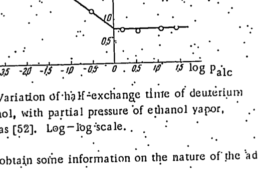


Fig. 34. Variation of half-exchange time of deuterium with ethanol, with partial pressure of ethanol vapor, after Farkas [52]. Log−log scale.

TABLE 48

Variation of $\tau_{1/2}$ for the Exchange with Hydrogen Pressure

p_{H_2}, mm Hg	$\tau_{1/2}$, min
2	4.1
7	5.5
20	6.5

On the basis of these results, and of a comparison with the rate of the ortho−para conversion under the same conditions, the authors conclude that mutual displacement of hydrogen and alcohol from the catalyst surface occurs, and obtain some information on the nature of the adsorption isotherms for catalyst surfaces

In principle, by studying the influence of various factors on the observed constant rates of heterogeneous exchange, it is possible to find the true kinetic equations and the nature of the determining stages, but the analysis in such cases is more complex and the results are not as conclusive as for homogeneous exchange.

The above examples give some idea of the methods for determination of the true kinetics of isotopic exchange from the rate constants. Such investigations play an outstanding role in establishing the mechanisms of exchange reactions and in studying the relationship between reactivity and chemical structure. Such measurements can also be used for determination of a number of physicochemical constants − activity coefficients, solubilities, etc.

LITERATURE CITED

[1] H. Gest, M. E. Kamen and J. M. Reiner, Arch. Biochem. 12, 273 (1947). V. Linnenbom, Radioactivity.

Applied to Chemistry, edited by Wahl and Bonner, Moscow, Foreign Lit. Press, p. 72 (1954).

[2] C.W. Sheppard and A.S. Householder, J. Appl. Phys. 22, 510 (1951); C.W. Sheppard, Ibid, 19, 70 (1948).

[3] A.K. Solomon, J. Clin. Invest. 28, 1297 (1949).

[4] G. Friedlander and J. Kennedy, Introduction to Radiochemistry, Moscow, Foreign Lit. Press (1952).

[5] R.B. Duffield and M. Calvin, J. Am. Chem. Soc. 68, 557 (1946).

[6] O. Myers and R. Prestwood, Radioactivity Applied to Chemistry, edited by Wahl and Bonner, Moscow, Foreign Lit. Press, p. 11 (1954).

[7] R. Barrer, Diffusion in and through Solids, Moscow, Foreign Lit. Press (1948); W. Seith, Diffusion in Metallen. Berlin; 1939; Jui Hsin Wang, Radioactivity Applied to Chemistry, edited by Wahl and Bonner, Moscow, Foreign Lit. Press, p. 56 (1954); A.N. Murin, Proc. Acad. Sci. USSR 74, 65 (1950); A.N. Murin and B. Lurye, Proc. Acad. Sci. USSR 73, 933 (1950).

[8] S.Z. Roginsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 601 (1940).

[9] J. Mayer and M.G. Mayer, Statistical Mechanics, Moscow, Foreign Lit. Press (1952).

[10] L. Landau and E. Lifshits, Statistical Physics, Moscow, State Tech. Press (1951).

[11] D.N. Kursanov, V.N. Setkina and O.D. Sterligov, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 6, 1035 (1953).

[12] N.M. Dykhno and A.I. Shatenshtein, J. Phys. Chem. 28, 14 (1954).

[13] A.I. Shatenshtein and Ya.M. Varshavsky, Proc. Acad. Sci. USSR 85, 157 (1952).

[14] N.E. Brezhneva and S.Z. Roginsky, Progr. Chem. 7, 1503 (1938).

[15] F. Paneth, Radioelements as indicators and other selected topics in inorganic chemistry. London, 1928; F. Paneth, Z. Elektrochem. 28, 113 (1922); F. Paneth and W. Vorwerk, Z. phys. Chem. 101, 445 (1922).

[16] O. Hahn, Applied Radiochemistry, Moscow, State Chem. Press (1947).

[17] H.A. Doerner and M. Hoskins, J. Am. Chem. Soc. 47, 662 (1925).

[18] N.E. Brezhneva, S.Z. Roginsky and A.I. Shilinsky, J. Phys. Chem. 9, 752 (1937).

[19] J.M. Wilson and R. Dickinson, J. Am. Chem. Soc. 59, 1358 (1937).

[20] H.A.C. McKay, Nature 142, 997 (1938).

[21] H.A.C. McKay, J. Am. Chem. Soc. 65, 702 (1943).

[22] J. Barnes, W. Burgus and J. Miskell, Radioactivity Applied to Chemistry, Chapter 8, Moscow, Foreign Lit. Press (1954); I.F. Horing, G. Levey and J.E. Willard, J. Chem. Phys. 20, 1556 (1952).

[23] E. Broda, Advances in Radiochemistry, Chapter 9, Moscow, Foreign Lit. Press (1952); Chien Willard, J. Am Chem. Soc. 75, 6160 (1953).

[23a] L. Landau and E. Lifshits, Quantum Mechanics, Part 1, Moscow–Leningrad, p. 490 (1948).

[24] D.I. Blokhintsev, Principles of Quantum Mechanics, 2nd Edition, p. 473 (1949).

[25] W.H. Johnston and C.J. O'Shea, J. Chem. Phys. 21, 2080 (1953).

[26] M.I. Temkin, J. Phys. Chem. 15, 296 (1941); N.I. Kobozev and Yu.M. Goldfeld, J. Phys. Chem. 10, 261 (1937).

[27] S.Z. Roginsky, Adsorption and Catalysis at Heterogeneous Surfaces, Moscow, Acad. Sci. USSR Press (1948); V.L. Bonch-Bruevich and F.F. Volkenshtein, J. Phys. Chem. 28, 1219 (1954); F.F. Volkenshtein, J. Phys. Chem. 21, 1317 (1947).

[28] V.N. Setkina, D.N. Kursanov and A.L. Liberman, Bull. Acad. Sci. USSR, Div. Chem. Sci. 109 (1954).

[29] A.I. Brodsky and I.I. Kukhtenko, J. Phys. Chem. 25, 920 (1951); A.I. Brodsky, G.P. Miklukhin, I.I. Kukhtenko and I.P. Gragerov, Proc. Acad. Sci. USSR 57, 463 (1947).

[30] V.N. Kondratyev, Spectroscopic Investigation of Gaseous Chemical Reactions, Moscow, Acad. Sci. USSR Press (1944).

[31] O.M. Todes and S.Z. Roginsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 381 (1946).

[32] S.Z. Roginsky, Proc. Acad. Sci. USSR 100, 939 (1955).

[33] D.A. Frank-Kamenetsky, Diffusion and Heat Transfer in Chemical Kinetics, Moscow, Acad. Sci. USSR Press (1947).

[34] V.G. Levich, Physicochemical Hydromechanics, Moscow, Acad. Sci. USSR Press (1952).

[35] O.M. Todes, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 483 (1946).

[36] S.Z. Roginsky and O.M. Todes, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 475 (1946).

[37] M.I. Temkin, S.L. Kiperman and L.I. Lukyanova, Proc. Acad. Sci. USSR 74, 763 (1950).

[38] A. Farkas and L. Farkas, Proc. Roy. Soc. A152, 124 (1935).

[39] K.H. Geib, Handb. d. Katalyse, 3, 36, 1943.

[40] R.Kh. Burshtein, J. Phys. Chem. 14, 1195 (1940).

[41] R.Kh. Burshtein, Acta Physicochim. URSS 8, 857 (1938).

[42] A.J. Gould, W. Bleakney and H.S. Taylor, J. Chem. Phys. 2, 362 (1934).

[43] H.S. Taylor and E. Smith, J. Am. Chem. Soc. 60, 362 (1938).

[44] L. Farkas and E. Wigner, Trans. Far. Soc. 32, 708 (1936); P. Fugassi and F. Daniels, J. Am. Chem. Soc. 60, 771 (1938).

[45] F. Daniels and P.L. Veltman, J. Chem. Phys. 7, 756 (1939); E.T. Lessig, J. Phys. Chem. 36, 2335 (1932); E.L. Vernon and F. Daniels, J. Am. Chem. Soc. 55, 922 (1933).

[46] J.B. Perry and F. Daniels, J. Am. Chem. Soc. 72, 424 (1950).

[47] G. Meyer and M. Kahn, J. Am. Chem. Soc. 73, 4950 (1951).

[48] J.W. Gryder and R.W. Dodson, J. Am. Chem. Soc. 73, 2890 (1951).

[49] O. Meyers and J. Kennedy, J. Am. Chem. Soc. 72, 897 (1950).

[50] E. Abel and K. Hilferding, Z. Phys. Chem. 136, 186 (1928).

[51] E.N. Guryanova, Ya.K. Syrkin and L.S. Kuzina, Proc. Acad. Sci. USSR 85, 1021 (1953), E.N. Guryanova and V.N. Vasilyeva, J. Phys. Chem. 29, 577 (1955); E.N. Guryanova and V.N. Vasilyeva, J. Phys. Chem. 28, 60 (1954).

[52] A. Farkas, Trans. Far. Soc. 32, 922 (1936); 33, 678 (1937).

[53] J. Horiuti and M. Polanyi, Nature 132, 819, 931 (1933); J. Horiuti and T. Kwan, Proc. Imp. Acad. (Tokyo); 15, 105 (1939).

[54-58]*

---

* These references, mentioned in the text, do not appear in the literature cited section of the original – Translator.

CHAPTER III

MECHANISMS AND STAGES OF ISOTOPIC EXCHANGE

The concept of isotopic exchange covers processes of varying degrees of complexity. In it are represented all the mechanisms met in elementary chemical reactions in addition to mechanisms which have no direct analogs in ordinary chemistry. Isotopic exchange can occur in one, two, or many stages; it may be heterogeneous or homogeneous. It may be based on transfer of electrons, protons, and larger charged and neutral groups; or on transfer of whole unchanged molecules or even more complex particles. The formation and rupture of chemical bonds in isotopic exchange may occur heterolytically (Fig. 35, b); i.e., without separation of electrons forming electron pairs in covalent bonds, or homolytically with separation of such pairs (Fig. 35, a).

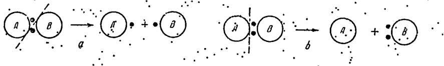


Fig. 35. Homolytic (a) and heterolytic (b) dissociation of a molecule AB.

Intermediate stages in isotopic exchange include dissociation of molecules into charged or uncharged particles, association, tautomeric intramolecular rearrangements, desorption, and evaporation. In addition to direct chemical interaction of saturated molecules with formation of intermediate collision complexes, isotopic exchange reactions proceeding by ionic and radical mechanisms are common.

Homogeneous and heterogeneous catalysis processes play an important role in isotopic exchange. In gaseous reactions the exchange is often localized at the walls of the reaction vessel; many isotopic exchanges are chain reactions. Isotopic exchange is accelerated and often induced by radiations, and in work with short-life radioactive isotopes the radiations of the isotopes themselves may influence the exchange. In the use of isotopes as tagged atoms it is necessary to understand clearly the diversity of mechanisms and manifestations of isotopic exchange. Otherwise it is easy to underestimate or miss its role in the changes of the isotopic composition of substances and phases, and to reach erroneous conclusions, ascribing to other processes changes induced by isotopic exchange. A differentiated approach to the mechanism of isotopic exchange is particularly important when the latter is used for investigations of reaction mechanisms and the chemical structure of compounds. In view of this, we shall consider separately the principal isotopic exchange mechanisms and the main stage sequences, starting with the simplest. The discussion will be based on the classification of isotopic exchange processes according to the nature of the transferred particles and of the intermediate active forms (Table 72, §23).

Whenever possible the reasoning and conclusions will be illustrated by examples which demonstrate the range of applicability of the views put forward and the difficulties which are met in attempts to establish mechanisms with certainty. Special attention is devoted to hydrogen exchange and halogen exchange, which are the best studied groups of isotopic exchange reactions and which have played a leading role in theoretical development of the subject.

§ 1. Exchange by Electron Transfer

When atoms of a particular element can exist as ions with different charges, a peculiar mechanism is possible in which a change of isotopic composition does not require direct transfer of atoms of a given isotope between molecules, but is in the final analysis effected by transfer of electrons only. This type of exchange is found fairly often, and under favorable conditions the rates of the processes may be very high.

Numerous examples are given in Haissinsky's review [1]. As an illustration, we return to the already familiar

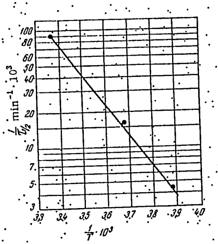


Fig. 36. Effect of temperature on the rate of Ce^{3+}/Ce^{4+} exchange in 6 M HNO_3 solution [3]. $[Ce^{3+}] = [Ce^{4+}] = 2\cdot 10^{-3}$ M; $E_{act} = 11.7$ kcal/mole.

isotopic exchange between tri- and quadrivalent cerium ions in nitrate and perchlorate solutions (see §8, Chapter II). By mixing acid solutions of trivalent and quadrivalent cerium nitrates, one of which contains radioactive cerium (for example, Ce^{144} with a half-life of 275 days), and after some time, separating the quadrivalent salt from the trivalent by extraction with ethyl ether, it is easy to show that the radioactive isotope is present both in the ethereal extract and in the remaining aqueous solution [2]. By carrying out the extractions and radioactivity determinations at definite time intervals it is possible to study the exchange kinetics. As Fig. 36 shows, the rate constant varies exponentially with the temperature. The slope of the line in this figure corresponds to an activation energy of about 12 kcal/mole [3]. The combined results show that the process under considera- tion reduces to a change in the charges of the tri- and quadrivalent ions, effected by electron transfer is shown in Equation (1).

$$\overset{\ominus}{\curvearrowright}\; Ce^{3+} + \overset{*}{C}e^{4+} \longrightarrow Ce^{4+} + \overset{*}{C}e^{3+} \tag{1}$$

The asterisk indicates that the radioactive isotope was added to the quadrivalent cerium before the experiment.

The process is greatly accelerated by even very low concentrations of fluoride ions. Without fluoride ions, in 6 N HNO_3 solutions and 0.002 N concentrations of Ce^{3+} and Ce^{4+} ions, the half-conversion time for reaction (1) is approximately 10 minutes. In absence of F^- the temperature coefficient of the reaction rate, insensitive to $[H^+]$, is 7.7 kcal/mole.* The reaction order is unity with respect to Ce^{3+} and somewhat less than unity with re- spect to Ce^{4+}. The rate of the process can be varied in wide limits by varying the temperature, concentrations of the components, and the solution acidity.

The relationships described for cerium ions are typical for the exchange of simple ions, but with other con- ditions equal, the absolute rates can vary greatly according to the value of F. In particular, isotopic exchange between ions of bi- and quadrivalent tin, uni- and trivalent thallium, and bi- and trivalent europium by the elec- tron transfer mechanism is much slower, under equal conditions, than in the case of cerium ions. On the other hand, the exchange between univalent and bivalent mercury ions is considerably more rapid. According to recent data this is also true for isotopic exchange between ferrous Fe^{2+} and ferric Fe^{3+} ions. All cations are solvated in solution, and therefore in reality the electron transfers in all these cases occur between cation solvates, and in aqueous solutions between cation hydrates. Many instances of isotopic exchange of this type have also been de- scribed for polyatomic anions and also for complex ions. For example, the manganate ion exchanges with the permanganate ion, at a rate which for a long time eluded measurement, according to the equation

$$MnO_4^{2-} + \overset{*}{M}nO_4^{-} \rightarrow MnO_4^{-} + \overset{*}{M}nO_4^{2-}. \tag{2}$$

Recently Sheppard and Wahl [4] succeeded in overcoming the experimental difficulties involved, and ob- tained the first reliable quantitative data on the kinetics of this interesting reaction. The process was carried out near 0°C in dilute solutions, with the reaction commenced by an automatic procedure, and terminated by addi- tion of suitable reagents to the vigorously stirred solution. For the rapid separation of permanganate from man- ganate, necessary to measure the exchange, the authors used extraction of MnO_4^- by means of a solution of tri- phenylsulfonium bromide in chloroform and coprecipitation with tetraphenylarsonium perchlorate or perrhenate. Fig. 37 shows the kinetic curves in $1-F$ and t coordinates, rectified by logarithmic plotting. When the total con- centration of the two manganic acid anions was changed from $9\cdot 10^{-5}$ to $4.9\cdot 10^{-4}$ M, the half-conversion time

---

*Comparison with E in Fig. 36 shows a decrease of E by 4 kcal/mole.

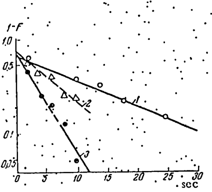


Fig. 37. Kinetics of isotopic exchange of manganese between MnO_4^- and MnO_4^{2-}, after Sheppard and Wahl, for different total concentrations of the exchanging manganese anions. 1) concentration of $[MnO_4^-] + [MnO_4^{2-}] = 9 \cdot 10^{-5}$ M; half conversion time $\tau_{1/2} = 12$ sec; 2) [illegible]$\cdot 10^{-4}$ M; $\tau_{1/2}$ [illegible] 6 sec; 3) $3.9 \cdot 10^{-4}$ M; $\tau_{1/2}$ [illegible] sec

fell from 12 to 3 seconds. It is clear that in concentrated solutions $\tau_{1/2} < 1$ second, and determinations in such solutions would be difficult. The results confirm the validity of the earlier work of Bonner and Portratz [5], which at one time had been doubted.

Isotopic exchange reactions effected by electron transfer are not confined to ions of like sign. Exchange may occur in the same way between a neutral and a charged particle or between ions with unlike charges. An example of reactions of the first type is the recently studied extremely rapid isotopic exchange of chlorine between gaseous ClO_2 and ClO_2^- anions in aqueous solutions [5]. In this case there can hardly be any doubt concerning the electronic mechanism, as all the exchange reactions of chlorine involving changes in the compositions of the ions, such as exchange between ClO_3^- and ClO_4^-; or between Cl^- ions and ClO_2, proceed slowly.

Isotopic exchange reactions which reduce to electron transfer form the first class of our classifications, which is given in expanded form at the end of this chapter. Up to the present, no one has succeeded in direct observation of the course of isotopic exchange by this mechanism without preliminary separation of the two exchanging chemical species, although this is possible in principle. Therefore, the accepted methods which have been developed for studying fact reactions have so far not been applied to such reactions. There also have not been any deliberate attempts to apply the advantages of the dynamic technique described in Chapter II, therefore reactions with $\tau_{1/2}$ of less than a few seconds are at present classified as instantaneous. Nevertheless, the kinetics of ordinary elementary reactions in solution have often been studied for $\tau_{1/2}$ of thousandth or even millionth parts of a second, and even more rapid processes have been successfully studied*. A considerable extension of the measurement range in the direction of high rates is important for the theory of isotopic exchange with electron transfer. As yet, it has not proved possible even to measure the rate of isotopic exchange of the ferricyanide anion with the ferrocyanide anion, although $\tau_{1/2}$ for this process at room temperature is hardly less than 0.1 second.

$$[Fe^*(CN)_6]^{3-} + [Fe(CN)_6]^{4-} \rightarrow [Fe^*(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \qquad (3)$$

§ Tunnel and Nonadiabatic Transfers

Very surprisingly, in some instances such large and stable ions as the anions of manganic acids or ferricyanides exchange more rapidly than simple ions, and the exchanges proceed with very low activation energies. In such cases, in view of the high stability of the ions, it is natural to seek special mechanisms to explain the rapid electron transfers between the central atoms of the complexes, i.e., at relatively large distances and through molecules. Many authors assume the existence, in such cases, of tunnel transfers, which constitute a special type of process predicted and explained by quantum mechanics.

According to the classical mechanics, to overcome the energy barrier a particle should have energy equal to or greater than the height of the barrier. According to wave mechanics, the motion of particles is analogous to the motion of a radiation wave, and waves at least partially penetrate into any obstacle and, depending on its thickness, some part of radiation passes through the obstacle. In a similar way the particles leak through the energy barriers at energies insufficient to surmount them; this is called tunnel transfer (Fig. 38).

This is the mechanism by which α-particles are ejected from nuclei of radioactive substances, electrons are detached by high gradient electric fields from cold metals, etc.

---

*This question is discussed in a report of a conference of the Faraday Society on the subject of fast chemical reactions (Disc. Far. Soc., N 17. The Study of Fast Reactions, 1954).

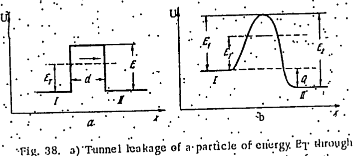


Fig. 38. a) Tunnel leakage of a particle of energy E_T through a rectangular barrier of width d, with equal energies for the initial (I) and final (II) states; b) similar scheme for a narrowing barrier in an exothermic process; U) internal energy; E_1 and E_2) activation energies of the forward and reverse reactions in adiabatic transition; $Q = E_2 - E_1$) heat of reaction.

The probability of tunnel leakage of a particle falls sharply with increasing width of the potential barrier and increasing particle mass, and increases with increase of the energy liberated in the reaction. The actual mathematical relationship between these quantities depends on the form of the barrier. The permeability of the simplest rectangular barrier [6] to tunnel leakage of particles is given by the equation

$$D = e^{\frac{-4\pi}{h}\sqrt{2m}\sqrt{U-E}\,d} \qquad (4)$$

where m is the mass of the particle and d is the width of the barrier; for barriers of other shapes this is replaced by l, the width of the barrier at the height of the leakage.

According to Equation (4), the probability of the transfer depends on the height of the barrier E_1 and of the position of the final level relative to the zero level. Fig. 38 shows that the energy difference between these two levels represents the energy effect Q of an exothermic process effected by the tunnel mechanism.

Expressions for the permeability of barriers of other shapes have also been calculated [6]. In all cases the probability Γ of transfer by the tunnel mechanism is equal to the product of D and a certain frequency ω, the physical meaning of which is not considered here.

$$\Gamma = \omega D = \Omega e^{-\alpha\sqrt{m}\,l}, \qquad (4a)$$

Formula (4a) shows that Γ greatly depends on the mass of the particle transferred by the tunnel mechanism. Under equal conditions, the less the particle mass, the greater are the distances to which the action of the tunnel mechanism extends. For a given D, ω is inversely proportional to $\sqrt{m}$. Tunnel transfers play an important part in electron transfer in ordinary chemical reactions with very small energy changes. In a few exceptional instances they must be taken into account as small corrections in proton transfer [7]. In all other cases the transfer is effected by the classical mechanism of surmounting the barrier; this may be either adiabatic or nonadiabatic [8].

A combination of electron transfer with transfers of heavy particles such as atoms, radicals, or molecules is required to bring about many chemical reactions. In such cases, because of the great difference between the masses of electrons and atoms, peculiar differences arise in the synchronization of their transitions, expressed by the Franck-Gondon principle [9], which has very extensive applications. By this principle, during the transition of an electron from one position to another, atoms do not have time to change their positions Therefore, in particular, in the optical excitation of an electron in a diatomic molecule the atoms of which are at a distance R_0^1, i.e., at the lowest point (trough) of the $U = U(R)$ potential energy curve (Fig. 39), the system enters, not the minimum energy position R_0^2 of an excited molecule (Fig. 39), but the position $R^* = R_0^1$. This requires the expenditure of additional energy $E = U^x_{exp} - \Delta U_0$, which remains in the excited molecule in the form of excess vibrational

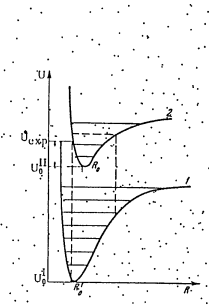


Fig. 39. Electron excitation scheme by the Franck–Condon principle. The lower Curve 1 corresponds to a normal molecule in its lowest electronic state; the upper Curve 2 represents an electronically excited molecule. The experimental excitation energy $\mathring{U}_{exp} > \Delta U_0 = U_0^{II} - U_0^{I}$.

energy. In relation to electron transfer in isotopic exchange of ions, the Franck–Condon principle may lead to the appearance of activation energy in processes which occur by a tunnel mechanism. At the same time, the heat effect of the aggregate process of isotopic exchange will be zero. The solvate layers of ions of different valencies have different structures, and the energy of their formation differs. Therefore, in particular, the Ce^{3+} and Ce^{4+} ions in the process discussed above have different hydrate layers. The zero heat effect presupposes not only electron transfer from Ce^{3+} to Ce^{4+}, but reconstruction of the hydrate layer of the trivalent ion into the quadrivalent type, and conversely.

Since the reconstruction involves displacement of solvent molecules, it does not have time to occur during the electron transfer, and the latter becomes impossible without a preliminary expenditure of energy, corresponding at least to formation of anomalous Ce^{3+} structures in the hydrate layers of Ce^{4+}, and of Ce^{4+} in the Ce^{3+} hydrate layers. This accounts for the origin of the activation energy and for the slowness of isotopic exchange by a tunnel mechanism for the reactions

$$Eu^{2+} + \overset{*}{E}u^{3+} \rightarrow Eu^{3+} + \overset{*}{E}u^{2+}; \qquad (5)$$

$$Tl^{+} + \overset{*}{T}l^{3+} \rightarrow Tl^{3+} + \overset{*}{T}l^{+} \qquad (6)$$

and many others. The position is changed substantially when the structure of the internal region of a complex ion is very stable and quite analogous for the two valency states, as in Reactions (2) and (3). In such cases almost no energy is required for reconstruction, and tunnel transfer becomes possible without expenditure of activation energy. This is Libby's explanation [10] for the rapidity of isotopic exchange in the most stable complex ions, and the slowness in simple ions with unstable solvate layers.

Apparent exceptions are the instantaneous exchange of bi- and univalent mercury ions and the extremely slow exchange of bi- and trivalent cobalt hexammines. As will be shown later, the first of these reactions

$$\overset{*}{H}g^{2+} + Hg_2^{2+} \rightarrow Hg^{2+} + \overset{*}{H}g_2^{2+} \qquad (7)$$

proceeds by a very peculiar stage mechanism and essentially belongs to another type; as regards the second reaction

$$[Co(NH_3)_6]^{2+} + [\overset{*}{C}o(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{3+} + [\overset{*}{C}o(NH_3)_6]^{2+}, \qquad (7a)$$

according to Biltz [11] the two cobalt complexes involved have different structures, and, in particular, the $Co^{2+} - N$ distance is approximately 2.5 Å, while the $Co^{3+} - N$ distance is only 1.9 Å, so that the first complex is much less stable than the second. Energy must be therefore expended for reconstruction and the kinetic picture is typical of simple solvates and not of stable complex ions. Thus it is possible within the framework of Libby's theory to attempt to explain the slowness of the isotopic exchange of the two cobalt hexammines, which is one of the slowest known isotopic exchange reactions in solution to proceed by the electron transfer mechanism.

Particular symmetry and stability is found in the heterocyclic porphin structure, formed by the linking of four pyrrole rings through methylene groups. Porphin forms the basis of most animal and plant respiratory pigments, and also of the most important cell enzymes (cytochromes). In the center of such a structure, the hemins have an iron atom, the chlorophylls a magnesium atom, and the pinnoglobins of molluscs a manganese atom. Further differences between the cytochromes are caused by the nature of the side groups (Fig. 40) and also by the nature of the protein carrier. Because of these properties of the porphin nucleus, the electronic mechanism suggested for stable inorganic complexes should be effected especially easily in the cytochromes. The as yet scanty

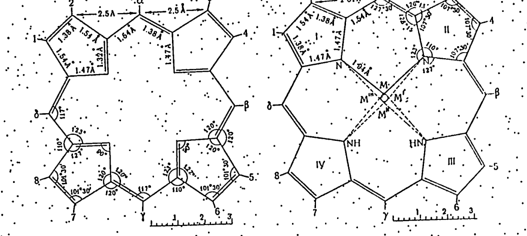


Fig. 40. Scheme of porphin ring structure. Left, structure with twelve double bonds without a central atom; Right, structure with ten double bonds and a central metal atom. The scale in angstroms is shown below.*

available data on isotopic exchange of biocatalysts do not appear to contradict this view.

It would be erroneous to regard the above mechanism as specific for isotopic exchange. Tunnel transfer is one of the possible mechanisms for any exothermic oxidation of ions proceeding by an electron transfer mechanism; and the higher the Q for the reaction, the higher the probability of such a process.

In tunnel transfer between large ions the electron has to be transferred over considerable distances. For example, the distance from the center of the metal atom to the edge of the porphin ring is 3.5 Å, and with two such rings an electron must travel about 7 Å. This raises the question of the distances at which the tunnel mechanism can operate. Here it is necessary to consider another peculiar quantum-mechanical effect which has been extensively studied for ions and excited atoms in the gas phase. The average distances over which electron transitions of the type

$$\left.\begin{array}{l} {}'\overset{\ominus}{Me}{}^{+} + {}''Me \longrightarrow {}'Me + {}''Me^{+} \\ {}'Me^{n+} + {}''Me^{(n-1)+} \longrightarrow {}'Me^{(n-1)+} + {}''Me^{n+} \end{array}\right\} \qquad (8)$$

or excess excitation energy transfer between molecules

$$'\check{M} + {}''M \rightarrow {}'M + {}''\check{M} \qquad (9)$$

($\check{M}$ represents the electronically excited state) occur are usually represented by the so-called transition diameters, which are analogous to the molecular diameters in the kinetic theory of gases for ordinary collisions. Experiments on ionic overcharging, on extinction of fluorescence, and other observations have shown that the transition diameters increase very sharply if the particles between which electrons or excitation energy are transferred have similar energy levels. This similarity plays the same role as resonance in the transfer of sonic vibrations or the oscillations of a pendulum.

Resonance is naturally at a maximum when the process involves particles of the same chemical composition, as in Equation (8), with ions and atoms of the same element. Thus, for example, in an investigation of the depolarization of fluorescence radiation of sodium vapor excited by linearly polarized light, effective radii 10,000

---

* The primes indicate different vibration types of the central metal atom

[illegible] as large as the already large gas-kinetic radii of sodium atoms were found for the transfer of energy from excited to nonexcited sodium atoms [12]. Similar effects are also found in electron transfer. For example, the effective cross sections for the reaction

$$He^{+} + Ne \rightarrow He + Ne^{+}$$

[illegible] of [illegible] ev greatly exceed the effective cross sections for the reaction

$$He^{+} + A \rightarrow He + A^{+}$$

[illegible] ev. For electron transfer between two isotopic atoms

$$Me^{+} + \overset{*}{Me} \rightarrow Me + \overset{*}{Me}{}^{+} \qquad (9a)$$

the effective radii may reach 10^2 A.

The probability of tunnel transfer of electrons in relation to the distance and the type of structure of the electron shells of atoms has been considered by numerous authors. Libby [10] gives numerical data for the electron transition frequency in the H_2^+ molecule and in an analogous hypothetical particle formed by two ions with incomplete 3d shells and with charge ze at each ion (Table 49). The first values are given in terms of Bohr radii a_0 = [illegible] A. To convert these to A, R must be multiplied by this value, or, as a rough approximation, divided [illegible]. Fig. 11 shows the exchange frequency as a function of the distance in a molecular hydrogen ion and in an analogous molecule formed by two A^{z+} ions with z gaps in the d shell, for z = 1 and z = 2. The figure and the table show clearly that the presence of 3d electrons greatly increases the probability of transition at large distances and that probability decreases with increasing z. At a distance of the order of $40a_0$, i.e., ~20 A, even for [illegible] the ratio ν/ν_0 is $\sim 10^{-8}$, i.e., ν is approximately $6.6 \cdot 10^7$ sec^{-1}. In other words, such transitions may occur [illegible] ions involved in isotopic exchange at distances considerably in excess of atomic distances. Libby and other authors have applied this method also to solutions on the assumption that the order of magnitude should not change. Until recently the theory of electron transfer in liquid media was not sufficiently well developed for quantitative calculations and unequivocal conclusions. Recently Weiss [13] in a detailed investigation, has attempted to surmount the existing difficulties. Considerable interest attaches to the work of Eyring et al. [14] on electron transfer in solutions. Tunnel leakage and nonadiabatic transfers with intersection of potential energy surfaces are examined separately. It is pointed out that the fundamental characteristics of exchange with electron transfer cannot be explained by the influence of the charges of the exchanging ions, ionic strength of the solution, or the dielectric constant of the medium, and great importance is attached to the effects which result in sharp differences in the entropy factors of the rate constants of reactions with large and small activation energies. In the first case the entropy of activation $S^{\#}$ is negative, and in the second, positive. In the example of Ce^{+3}/Ce^{+4} isotopic exchange discussed above, both processes occur in parallel, and for E = 7.7 kcal/mole $S^{\#}$ = 40, while for E = 24 kcal/mole $S^{\#}$ = −25, i.e., the difference $\Delta S^{\#}$ between the two reaction routes is 65 kcal/mole · degree.

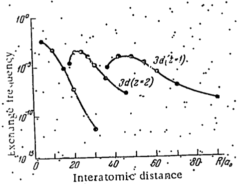


Fig. 11. Variation of the dimensionless frequency of electron transfer between nuclei with the distance, after Libby [10]. Left-hand curve for H_2^+, right-hand and middle curves for A_2^{z+} particle.

The observed rate constants k_{obs} may be written in the form of the product of a rate constant for an ordinary adiabatic reaction and the probability ω_e of electron transfer at optimum configuration

$$k_{obs} = k_{ad} \cdot \omega_e \cong kT/h \cdot \exp\,[S^{\#}/R - H^{\#}/RT]. \qquad (10)$$

TABLE 49

a) Transition Frequencies of 1s-Electron in the H_2^+ Molecule, after Libby

R/a_0	ν/ν_0
5	0.0042
10	$5.9 \cdot 10^{-4}$
15	$5.7 \cdot 10^{-6}$
20	$5.0 \cdot 10^{-8}$
30	$4.0 \cdot 10^{-12}$

b) Transition Frequencies of a d-Electron for an A^{z+} A^{z+} Molecule

$zR/3a_0$	ν/ν_0	$zR/3a_0$	ν/ν_0
10	$3.4 \cdot 10^{-3}$	18	$2.0 \cdot 10^{-5}$
12	$1.0 \cdot 10^{-5}$	20	$2.7 \cdot 10^{-6}$
14	$9.7 \cdot 10^{-5}$	23.3	$1.2 \cdot 10^{-6}$
16	$7.1 \cdot 10^{-5}$	30	$4.4 \cdot 10^{-9}$

Hence the observed thermodynamic activation potential is

$$\Phi^{\#}_{obs} = -RT \ln k_{obs} = \Phi^{\#}_{ad} - RT \ln \omega_e \text{ и } S^{\#}_{obs} = S^{\#}_{ad} + R \ln \omega_e. \qquad (11)$$

Both in $\Phi^{\#}_{ad}$ and in $S^{\#}_{ad}$ the principal terms are Coulomb terms, associated with reconstruction of the solvate layers of the exchanging ions before the electron transfer. At small values of $H^{\#}_{obs}$ and negative $S^{\#}_{obs}$ this transfer occurs at relatively large distances r without alteration of the number of solvent molecules in the first solvate envelope of the ions. At $H^{\#}_{obs}$ and $S^{\#}_{obs} > 1$, the transfer is preceded by close approach of the ions with liberation of n molecules of solvent, which increases the entropy by $n \cdot \Delta S^{\#}_{f}$. If the $\Delta S^{\#}_{f}$ for the entropy of fusion of one mole of water is taken as 5.3, $\Delta S^{\#}_{obs}$ can be used to determine n. For the transition $Ce^{+3} \rightarrow Ce^{+4}$ $\Delta S^{\#}_{f}$ is found to be 12.

Mutual compensation of a number of factors brings the values of $\Phi^{\#}_{coul}$ and $\Phi^{\#}_{trans}$ for different reactions closer together, and therefore the differences between their rate constants are largely determined by $\Phi^{\#}_{cl}$ – RT ln ω_e. For a triangular barrier the values of ω_e^{tr} are calculated. The ratio $\omega_e^{tr}/\omega_e^{rect}$ is calculated from the formula

$$\omega_e^{tr}/\omega_e^{rect} = 4 \exp\,[-4\pi/3h\,(mE)^{1/2} \cdot l], \qquad (12)$$

where E is the height of the barrier, and l is its variable width for tunnel leakage. Calculation with zero-point energy and electrostatic terms taken into account leads to an expression for the optimum value of l at which electron transfer occurs

$$l^2_{opt} = 3en_A n_B h \cdot r_0^{1/2} / 8\pi kTD \cdot (m \cdot n_C)^{1/2}, \qquad (13)$$

where n_A and n_B are the total charges of the exchanging solvated ions; n_C is the positive charge of the central ion receiving the electron, D is the dielectric constant of the medium, $r_0 = n^2_{eff} a_0$ is the classical orbit radius of the transferred electron, n_{eff} is its effective principal quantum number, a_0 is the Bohr orbit radius. The authors calculated $\Phi^{\#}_{cl}$ and $\Phi^{\#}_{coul}$ and taking for all the reactions in question $\Phi^{\#}_{trans}$ = 8.1 kcal/mole, found $\Phi^{\#}_{theor}$ which was compared with $\Phi^{\#}_{exp}$ (see the last table of the Appendix).

In this theory electron transitions in intermolecular oxidation – reduction processes are regarded as intramolecular, occurring in a symmetrical intermediate complex, with equalization of the structure of the solvate envelopes of the exchanging ions. This is assisted by "collectivization" of some of the molecules (or ions) of the coordination medium with formation of intracomplex "bridges". This model was introduced by Taube [15a] and confirmed by investigations of the oxidation of bivalent chromium. After the electron transfer the symmetrical complex decomposes with a new distribution of the molecules (or ions) of the solvate layers. It was shown by experiments with radioactive chlorine Cl^{36} that ions of an intracomplex bridge are capable of "changing hosts" without exchanging isotopically with the free ions of the solution [15b].

§3. Catalytic Action of Negative Ions on Isotopic Exchange of Cations

One remarkable feature of the mechanism under consideration is the high sensitivity of the isotopic exchange rate to small concentrations of ions of the opposite sign. In particular, the rate of exchange between positive ions with the same charges should greatly increase in presence of negatively charged simple ions. Some authors assume a different mechanism for acceleration of isotopic exchange in systems in which the exchange rate R is directly proportional to the first power of the concentration of a foreign anion (for example, a halide ion) and in systems in which this rate is proportional to other, higher orders of Hal^- concentration. Very often the rate is at the same time inversely proportional to some power of the hydrogen ion concentration, for example $[H^+]^2$, or the square root of that concentration

$$\left.\begin{aligned} &a)\quad R\sim\frac{[Hal^-]^n}{[H^+]^m};\\ &b)\quad R\sim\frac{[Hal^-]^n}{[H^+]^{1/2}}\\ &n=1;\ 2;\ \ldots\\ &m=1;\ 2;\ \ldots\end{aligned}\right\}\qquad(14)$$

For the first type of acceleration n = 1, and for the second type it is two, three, or an even larger whole number. For a reaction with n = 1, a very peculiar mechanism of stabilization of the hydrate layers of two positive ions by joining them with the aid of a Hal^- or OH^- ion into a single common and more stable layer, as shown in Fig. 42, is postulated. The structure of ordinary unstable complexes then approaches that of stable complexes, for which E is lower and the transition rate by the tunnel mechanism is higher.

This is the explanation which has recently been given for the catalysis of exchange between cerium ions by F^- ions, the catalysis of exchange between europium ions by Cl^- ions, etc. According to Taube, the molecules which form the links act as zones of increased permeability to tunnel transitions of electrons.

A different mechanism is assumed for the catalytic action of negative ions on isotopic exchange in thallium, tin, and certain other ions, when R is proportional to higher powers of the chloride ion concentration, and therefore the catalytic effect is particularly strong. As an example, we shall consider isotopic exchange between Tl^+ and Tl^{3+}, according to the data of Harbottle and Dodson [16]. The experiments were carried out with Tl^{204}, with a half-life $T_{1/2}$ = 2.7 years, in $HClO_4$ solution, which is widely used for such investigations as one of the strongest acids, the anion of which has no additional catalytic effects. Fig. 43 shows good conformity to an exponential law and increase of R and k with increasing concentrations of the exchanging ions

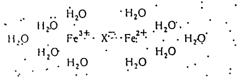


Fig. 42. Joining of Fe^{3+} and Fe^{2+} hydrates into a common system by means of a catalyzing X^- ion, after Libby [10].

$$Tl^+ + \overset{*}{T}l^{3+}\rightarrow \overset{*}{T}l^{3+} + \overset{*}{T}l^+. \qquad (15)$$

A comparison of the numerical values of the exchange constants for different values of $[Tl^+]$ and $[Tl^{3+}]$ indicates a first-order reaction with respect to the concentrations of the exchanging ions

$$R\approx k\,[\overset{*}{T}l^+]\,[Tl^{3+}]. \qquad (16)$$

Very sharp and peculiar effects are produced by addition of Cl^- ions or replacement of part of the $HClO_4$ by HCl. In Fig. 44 the broken line shows the value of log k at $[Cl^-] = 0$. It is clear from the graph that the first very small concentrations of Cl^- ions diminish k tens of times. However, on further increase of $[Cl^-]$ the initial value of k is first restored, and k then continues to increase, reaching values tens of thousands times greater than the rate constant in absence of Cl^- ions. A comparison of the dependence of k on the concentration with results of spectrophotometric determinations on the same solutions leads to the conclusion that, in addition to slow direct isotopic exchange between hydrates on uni- and trivalent thallium, exchange also occurs between complexes of these ions formed with participation of Cl^-. Here $TlCl_2^+$ (and also possibly $TlCl^{2+}$) formed at low concentrations of Cl^- ions exchanges electrons more slowly with Tl^+ ions than do the simple Tl^{3+}_{aq} ions. On the other hand, $TlCl_4^-$ ions, which contain all the trivalent thallium, exchange electrons much more rapidly than to the Tl^{3+} ions at moderate and high Cl^- concentrations. It is further assumed that this exchange occurs mainly not with "bare" Tl^+_{aq} ions, but with $TlCl_3^{2-}$ and $TlCl_4^{3-}$ complexes, the formation of which in chloride solutions was proved long ago by Fromherz and Lih [17]. In this interpretation, Cl^- ions make the exchange of ordinary hydrated ions more similar to the exchange of stable symmetrical ions of the type of MnO_4^{2-} and MnO_4^-. From this point of view it is advantageous for the number of Cl^- ions in the complexes of ions of both charges to be the same, for example, $TlCl_4^-$ and $TlCl_4^{3-}$. It is not clear, however, whether the stability of complexes with Cl^- ions is really greater and the sensitivity to changes of charge of the central ion is less, than in hydrates of the same ions. This is doubtful for a difference of two units between the charges; and additional proof is needed of the possibility of reducing the catalytic action of Cl^- ions in such cases to a Libby mechanism. It is also not clear whether it is possible, with this composition of the chloride ion complexes, to obtain the observed relationships between k and $[Cl^-]$. The activation energy for the exchange in question is: without Cl^- ions E = 14.2 kcal/mole, in catalysis by Cl^- ions E_{obs} calculated from the ln k − (1/T) relationship, is still higher, reaching 29.6 kcal/mole. This does not agree well with a tunnel mechanism. In fact, for exchange between equilibrium species formed according to the equations

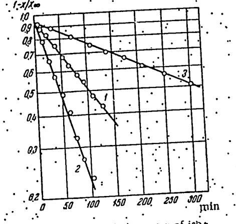


Fig. 43. Exponential character of isotopic exchange of Tl^+ with Tl^{3+} [16].

1) $[Tl^+] = 6.8\cdot10^{-4}M$; $[Tl^{3+}] = 1\cdot10^{-4}M$;
2) $[Tl^+] = 6.8\cdot10^{-4}M$; $[Tl^{3+}] = 1\cdot10^{-3}M$;
3) $[Tl^+] = 1.35\cdot10^{-4}M$; $[Tl^{3+}] = 1\cdot10^{-4}M$

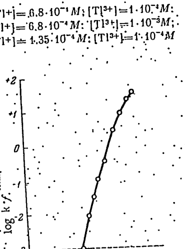


Fig. 44. Bilogarithmic plot of the rate constant $k\cdot f^{-1}$ against the Cl^- ion concentration [16].

$$\left.\begin{aligned} &a)\ Tl^+ + 3Cl^- \rightleftarrows TlCl_3^{2-}\\ &b)\ Tl^+ + 4Cl^- \rightleftarrows TlCl_4^{3-}\\ &c)\ Tl^{3+} + 4Cl^- \rightleftarrows TlCl_4^-\end{aligned}\right\}\qquad(17)$$

the concentration of any of the complexes, for example $[TlCl_4^{3-}]$, may be written as

$$[TlCl_4^{3-}] = K\,[Cl^-]^4\,[Tl^+] = K_\infty e^{Q/RT}\,[Cl^-]^4\,[Tl^+]. \qquad (18)$$

In calculations of the temperature dependence of the rate, the sum of the heats of formation of the complexes a and b participating in the electron exchange enters the value of E_{obs} and

$$E_{obs} = E_{true} - Q_a - Q_b \qquad (19)$$

or

$$E_{true} = E_{obs} + Q_a + Q_b. \qquad (19a)$$

In order that E_{obs} should be greater than E_{true}, Q_a and Q_b must be negative and K should be large.

In the present example both the active complexes formed with the catalytic Cl^- ions have charges of the same sign. In otherwise equal conditions, it would be more advantageous to have opposite signs in order to decrease electrostatic repulsion and to ensure a closer approach of the exchanging ions on collision. This is true both for a tunnel and for a nonadiabatic mechanism. However, the importance of Coulomb electrostatic repulsion and attraction in solutions should not be overestimated. The complete electrolytic dissociation of most salts itself indicates complete compensation of the energy of electrostatic attraction by energy of solvation. In the solvate layers the charges are shielded by dipole orientation. Therefore the ions in solvate layers are attracted considerably less strongly than free ions. Macroscopically, this corresponds to division of the electrostatic interaction potential by the dielectric constant of the solvent, which is 80 for water. Electrical repulsion is especially low between polyatomic and complex anions such as NO_3^-, SO_4^{2-}, $Tl(CN)_6^{3-}$ etc.. Therefore the tendency of certain authors to assume that electron transitions occur, as a rule, between oppositely charged ions formed reversibly in solutions cannot be regarded as substantiated. Such a mechanism is probably relatively rare. In particular, for the isotopic exchange between stannous and stannic chlorides in absolute alcohol, reported by Meyer and Kahn [18] and discussed in the previous chapter, the following stages are probable:

$$\left.\begin{array}{l}
\text{a)}\ \overset{*}{Sn}Cl_4 \rightleftharpoons \overset{*}{Sn}Cl_3^+ + Cl^- \quad \text{(rapidly established equil.)};\\
\text{b)}\ SnCl_2 + Cl^- \rightleftharpoons SnCl_3^- \quad \text{(rapidly established equil.)};\\
\text{c)}\ \overset{*}{Sn}Cl_3^+ + SnCl_3^- \rightleftharpoons \underbrace{Sn\overset{2\ominus}{\curvearrowright}\overset{*}{Sn}Cl_6}_{\text{intermed. compl.}} \rightarrow \underset{\text{slow det. stage}}{\overset{*}{Sn}Cl_2 + SnCl_4}.
\end{array}\right\} \qquad (20)$$

This scheme is based on the relationship between k and the concentrations of the chlorides; supplemented by data on the electrical conductivities of their solutions in alcohol.

Catalytic effects in the oxidation and reduction of cations in solution are not confined to the action of halide ions and OH^- ions. The catalytic action of solid catalysts such as platinum, manganese dioxide, etc., has been reported in the literature. This effect has been little studied experimentally, but it seems likely that its discovery for conductors which are electronic conductors is not accidental, and that electron carriers may act similarly also in homogeneous oxidation [19]. In particular, this is the mode of action of the easily oxidized I^- ions in the oxidation and reduction of iron ions, as reported by A.V. Pisarzhevsky and M.A. Rozenberg [20]

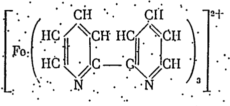
$$Fe^{3+} \overset{\ominus}{\curvearrowleft} + I^- \rightleftharpoons Fe^{2+} \overset{\ominus}{\curvearrowright} + I. \qquad (21)$$

It is evident that in mixtures of Fe^{2+} and Fe^{3+} ions the I^- ions will accelerate isotopic exchange, acting as electron carriers. Catalysis by this mechanism is probably very common and is often met in analytical chemistry.

There is no doubt that in recent years great advances have been made in investigations of the mechanism and kinetics of homogeneous isotopic exchange between ions of different valencies; however, the reliability and certainty of the results obtained should not be overestimated. We have already drawn attention to the difficulties which have arisen in the theoretical interpretation of electron transfers in solutions, yet equally great difficulties are involved in the separation of ions of different valencies from each other in order to observe the course of the exchange, as at present there are no methods for observing the distribution of a tagged isotope between ions of different valencies without prior separation. Because of the high sensitivity of electron transitions to the action of homogeneous and heterogeneous catalysts, apparently harmless separation operations often catalyze transition and create the appearance of rapid exchange where it does not exist. At the same time there are still no instantaneous or even very rapid methods for separation of isotopic substances, and therefore the rates of the most rapid isotopic exchange reactions cannot be measured. To illustrate the contradictions and errors caused by the difficulty of separation, we shall quote data on the kinetics of isotopic exchange between ferric and ferrous ions in solutions. This reaction is of great analytical, geochemical, and biochemical interest, and therefore it has been studied in detail by many authors.

§4. Isotopic Exchange Between Iron Ions

In the earliest investigations ferrous and ferric iron were separated by ether extraction from hydrochloric acid solutions, but, as was pointed out by Seaborg [21], this method gives high values for the exchange rate because of the strong catalytic action of HCl. At the beginning of the 1940's Nahinsky, working in the United States, used a chemical separation method and observed very rapid exchange, which was completed in a few seconds at room temperature in perchlorate solutions [22]. Van Alten and Rice [23] cast doubt on these results because of the possible catalytic effect of the reaction used for the separation, and studied the same process under similar conditions, separating Fe^{2+} and Fe^{3+} by diffusion through porous glass partitions by Northrop and Anson's method [24]. This method, applicable only to very slow processes, gave $\tau_{1/2} = 18.5$ for the exchange. Similar results were obtained by Kierstead [25] ($\tau_{1/2} = 39$ and 160 days) who used a similar method. However, Linnenbom and Wahl, and also Betts, Gilmour and Leigh [26] who used the same method, obtained a totally different result. The former found $\tau_{1/2} < 2$ hours, and the latter, $\tau_{1/2} \leq 30$ minutes. The question was clarified to some extent by the work of Dodson et al. [27], who developed a reliable chemical separation method. This method is based on the formation of very stable complexes between ferrous ions (in solutions buffered by CH_3COONa) and α,α'-dipyridyl; these do not participate further in the exchange and, in contrast to Fe^{3+} ions, are not precipitated by ammonia. The stability and reactivity of this complex were studied in detail by Baxendale and George [28]. The ferrous tri-α,α'-dipyridyl ion formed



remains in solution after precipitation of $Fe(OH)_3$ by ammonia. Using this separation method, Silverman and Dodson [29] made a detailed study of the kinetics of the reaction, which proved to be one of the fastest electronic exchange reactions of simple ions. Its rate constant was 10^6 times that found by Van Alten, and 10^7 times that found by Kierstead. According to the mechanism of joining and stabilization of the hydrate layers, the reaction is catalyzed by Cl^- and OH^- ions, and the activation energy for the exchange of different forms of trivalent iron, like the activation entropies, vary in relatively narrow limits (Table 50). The investigation was performed with Fe^{55} with $\tau_{1/2} = 3$ years:

TABLE 50

Energy and Entropy of Activation of Isotopic Exchange of Ferric with Ferrous Ions

Type of ferric ion	E, kcal/mole	ΔS, cal/degree · mole
Fe^{3+}	9.9	−25
$FeOH^{2+}$	7.4	−18
$FeCl^{2+}$	8.8	−24
$FeCl_2^+$	(9,7)	−20

Despite the thoroughness of this investigation and the improvements introduced into the experimental procedure, the results obtained cannot be accepted with complete confidence until they have been confirmed by some new and independent method.

The influence of the separation method on exchange is often so great that it is not possible to eliminate it completely; however, by determining F for different times and extrapolating $\log(1 - F)$ to $t = 0$, it is possible to determine the magnitude of the error introduced by the method of analysis. This question has been considered in more detail by Prestwood and Wahl [30] who showed how corrections should be made for exchange induced by separation and for incomplete separation [30]. This, like all similar methods, is applicable only if the effects which cause the errors are reproducible [22].

§5. The Reality of Direct Electron Transfers in Solutions

There is no fundamental distinction, in their inner mechanism and kinetics, between isotopic exchange of ions in solutions and oxidation – reduction reactions between dissimilar dissolved ions. In both cases electron transitions occur and tunnel and nonadiabatic transition mechanisms are assumed, in both cases similarity of the energy levels is favorable, the Franck–Condon principle is applicable, and negative ions have a strong catalytic effect. In both cases the formation of oppositely charged and highly symmetrical complexes is favorable, etc. In this connection we must mention the work of Robertson, Law and Gorin [31] who, in the oxidation reaction between Sn^{2+} ions and Fe^{3+} ions, on replacement of $HClO_4$ by HCl and introduction of small quantities of Cl^- ions, observed effects quite analogous to those found in the isotopic exchange of Tl^{+} with Tl^{3+}, discussed earlier.

The foregoing analysis of the mechanism and kinetics of isotopic exchange effected by electron transfer may seem excessively detailed if recent experimental work is disregarded, since, despite the extensive experimental data in good agreement with the theory of direct electron transfer put forward by L.V. Pisarzhevsky and G.N. Lewis, the possibility of such transfers in solutions has itself been doubted by some authors. Recently additional evidence of the reality of such transfer has been obtained. Ward and Weissman [32] used microwave spectra for this purpose. Several authors had previously showed, by means of microwave spectroscopy, the existence of a characteristic paramagnetic resonance spectrum consisting of 28 lines (Fig. 45) for negative naphthalene ions in tetrahydrofuran solutions. These lines are superfine structure components, arising as the result of interaction of the magnetic moment of an unpaired electron of the naphthalene ionic radical $[\dot{C}_{10}H_8]^-$ with protons of the condensed nucleus. On addition of uncharged naphthalene molecules to the solution the lines broaden and the maxima diminish. Therefore the unpaired electrons are retained, but the duration of their existence has decreased. The authors attribute this to the transition

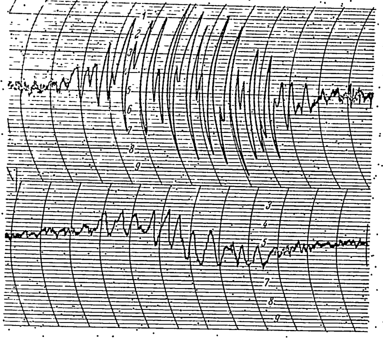


Fig. 45. Paramagnetic resonance spectrum of naphthalene ions (above) and the effect of naphthalene molecules on it (below), after Ward and Weissman [32].

$$\dot{C}_{10}H_8^- \rightarrow C_{10}H_8 + e \tag{21a}$$

and find for the average life of the $\dot{C}_{10}H_8^-$ ion at 30°C, at concentrations of naphthalene ions of $5 \cdot 10^{-4}$ M and of its molecules of 0.8 M $t = 1.2 \cdot 10^{-6}$ second. The rate constant for a bimolecular process is found to be $1 \cdot 10^{6}$ liter $mole^{-1} \cdot sec^{-1}$. These results would be more conclusive if the occurrence of instantaneous isotopic exchange in the process had been proved. Linschitz, Berry and Schweitzer [33] made a different approach to the same problem, and obtained important evidence for the formation of solvates of free electrons in the photo-oxidation of solidified organic liquids in the glassy state. If easily oxidized organic substances in mixed solvents, and alkali metals in methylamine are irradiated in such conditions, a characteristic absorption band is found in the infrared spectrum, attributed to solvated electrons $\dot{e}_{solv}$. In such systems slight softening is followed by luminescence of several hours' duration, which is attributable to recombination of the solvated electrons with the ionic radicals.

A combination of factors is in favor of this interpretation, but additional determinations of paramagnetic resonance and electrical conductivity would have been desirable to make the results conclusive.

These two examples are characteristic of the present state of the problem. Independent physical and chemical determinations confirm the physical reality of direct electron transfers in solutions. This is also indicated by the similarity, recently clearly demonstrated, of the electronic properties of organic and inorganic semiconductors, in which solid phase electron transitions and the ability of quasi-free electrons to move considerable distances are not subject to doubt. It may be noted that the use of optical methods for the detection of unusual forms is facilitated by decrease of temperature for such solids also. In particular, E.F. Gross [34] has recently succeeded in obtaining the absorption spectrum of Frenkel's exciton at the temperature of liquid helium.

§ 6. Isotopic Exchange Between Atoms and Simple Ions by a Dissociation Mechanism.

Isotopic exchange by a dissociation mechanism is probable in many cases. It has been definitely proved for a few systems, including molecular hydrogen in the gas phase [35].

The isotopic exchange of various initial molecular forms of hydrogen is represented by the equations

$$\left.\begin{array}{ll} \text{a)} & H_2 + D_2 \xrightarrow{k_1} 2HD; \\ \text{b)} & 2HD \xrightarrow{k_{-1}} H_2 + D_2; \\ \text{c)} & HT + D_2 \xrightarrow{k_2} DT + HD, \\ \text{d)} & DT + H_2 \xrightarrow{k_3} DH + HT \end{array}\right\} \tag{22}$$

etc. (See also § 13, Chapter I.)

In the gas phase in absence of catalysts any one of these reactions proceeds by a chain mechanism of a similar type, shown here for reaction (22, a):

$$\left.\begin{array}{ll} \text{a)} & H_2 \xrightarrow{k\,a} 2H; \\ \text{b)} & H + D_2 \xrightarrow{k\,b} HD + D; \\ \text{c)} & D_2 \xrightarrow{k\,c} 2D; \\ \text{d)} & D + H_2 \xrightarrow{k\,d} DH + H; \\ \text{e)} & H + D \xrightarrow{k\,e} HD. \end{array}\right\} \tag{23}$$

In addition, the reverse reactions must also be taken into account

$$\left.\begin{array}{ll} \text{f)} & H + H \xrightarrow{kf} H_2; \\ \text{g)} & D + D \xrightarrow{kg} D_2; \\ \text{h)} & H + HD \xrightarrow{kh} H_2 + D, \\ \text{i)} & D + HD \xrightarrow{ki} D_2 + H; \\ \text{j)} & HD \xrightarrow{kj} H + D \end{array}\right\} \tag{23}$$

The stage sequence 23, a–b–d, and 23, c–d–b, represent a "semidissociative scheme" in which the exchange is effected by interaction of atoms formed by dissociation of one of the H_2 or D_2 molecules with undissociated molecules of a different isotopic composition. The sequence 23 a–c–e represents an extreme dissociative scheme, in which first both the isotopically exchanging molecules dissociate into atoms, and then the dissociation products recombine differently.

For isotopic hydrogen exchange accurate measurements have been made of all the individual processes and of the effects of temperature on the rates and dissociation equilibria. It can be regarded as conclusively established that at not very high temperatures, when the degree of dissociation of hydrogen into atoms is not high, the process takes place practically only by the semidissociative scheme, and no part is played either by the complete dissociative scheme, or direct exchange of atoms between undissociated hydrogen molecules. At high temperatures, when the degree of dissociation into atoms is large and the equilibrium concentrations of free atoms become commensurable with the concentrations of the molecules, the complete dissociative scheme, including Stages 23, a [illegible] comes to play an appreciable part, and at the temperature of the electric arc (for example, in Langmuir's atomic torch) it may become predominant.

We shall examine in somewhat greater detail the kinetics of this well understood reaction of homogeneous exchange in the gas phase. Because of differences of mass and zero-point energy, the rate constants of the aggregate processes are unequal, and the rate constants of the elementary stages k_a and k_c, k_c and k_d, etc., are unequal also. The influence of these effects on the kinetic curves is relatively small, while the kinetic expressions are much more complicated, and therefore they will not be considered here, the isotopic exchange being assumed ideal. This is equivalent to assuming the identity of the thermodynamic and kinetic characteristics of hydrogen molecules of different isotopic compositions

$$k_1 \equiv k_2 \equiv k_3; \tag{24}$$

$$K_{diss} \equiv K \equiv K_{H_2} \equiv \frac{k_a}{k_f} \equiv K_{D_2} \equiv \frac{k_c}{k_g}. \tag{24a}$$

The rate constants for the atomic–molecular exchange are also assumed to be identical

$$k \equiv k_b \equiv k_d \equiv k_h \equiv k_i. \tag{24b}$$

With these far-reaching assumptions, if the degree of dissociation is low the equilibrium concentration of hydrogen atoms in the gas is constant, and is proportional to the square root of $p = p_{H_2} + p_{D_2} + p_{HD}$.

We denote the total concentration of molecular hydrogen by

$$[B_2] = [H_2]_t + [D_2]_t + [DH]_t = [H_2]_0 + [D_2]_0 = \text{const} \tag{25}$$

and the total concentration of atomic hydrogen by

$$[B]_t = [H]_t + [D]_t = [B]_0 = \text{const}; \tag{25a}$$

therefore

$$[B] = K_{diss}^{1/2} \cdot [B_2]^{1/2}, \tag{25b}$$

$$\left.\begin{aligned} [H] &= [B]\rho_H, \\ [D] &= [B]\rho_D, \end{aligned}\right\} \tag{26}$$

where

$$\left.\begin{aligned} \rho_H &= \frac{N_H}{N_H + N_D} \\ \rho_D &= \frac{N_D}{N_H + N_D}. \end{aligned}\right\} \tag{26a}$$

and

N_H is the total number of protium atoms in the system in the free and bound states, and N_D is the corresponding value for deuterium. It is evident that with an atomic–molecular mechanism the rate $R = k \cdot f(c)$ will be represented as

$$R = k[B] \cdot [B_2] = k \cdot K^{1/2} [B_2]^{3/2}. \tag{27}$$

The applicability of the kinetic equations for uncomplicated exchange to this case is evident, as each original molecule contains two atoms of an exchanging isotope, and each molecule of the product, two atoms of different isotopes. However, since the formation of intermediately substituted forms is excluded, we may use Equation (36) of Chapter II, writing it in the form

$$\ln(1 - F)\frac{[D_2]_0 \cdot [H_2]_0}{[D_2] + [H_2]} = -Rt. \tag{28}$$

If no HD molecules are initially present in the system

$$F = \frac{[HD]}{[HD]_\infty}. \tag{28a}$$

At constant composition, increase of the initial pressure increases $[B_2]$ linearly, and the numerator of the fraction in (28) quadratically

$$[H_2]_0 \cdot [D_2]_0 = \rho_H \rho_D [B_2]^2.$$

In view of this, and from Equations (27) and (28), r in the equation $1 - F = e^{-rt}$ will contain $[B_2]^{1/2}$ and the product $(\rho_H \rho_D)^{-1}$

$$r = kK^{1/2}\rho_H^{-1}\rho_D^{-1}[B_2]^{1/2}. \tag{29}$$

Thus, if the isotopic exchange obeys an exponential law, its true rate and R should increase in proportion to $[B_2]^{3/2}$, i.e., to $p^{3/2}$, while the values of r determined graphically should be proportional to $[B_2]^{1/2}$. The true order of the elementary exchange processes is two. The rates R and r, and also the value of k_{obs} calculated from them, contain the product

$$k_{obs} = k_{true} K_{diss}^{1/2}. \tag{30}$$

Since

$$k_{true} = k_{\infty\,true}\, e^{-E_{true}/RT} \tag{31}$$

and

$$K_{diss}^{1/2} = K_\infty^{1/2}\, e^{\frac{-Q_{diss}}{2RT}}, \tag{31a}$$

where Q_{diss} is the average dissociation energy of one mole of hydrogen, approximately 102 kcal/mole, it is evident that the experimentally determined activation energy of ideal isotopic exchange should be the sum of E_{true} and $\frac{1}{2}Q_{diss}$. In fact,

$$k_{obs} = k_{true} K^{1/2} = k_\infty^{obs} \cdot \exp\left[-\frac{E + 1/2\, Q_{diss}}{RT}\right] \tag{32}$$

Hence.

$$E_{obs} = E_{true} + \frac{1}{2}Q_{diss}. \tag{33}$$

or

$$E_{true} = E_{obs} - \frac{1}{2}Q_{diss}. \tag{33a}$$

Investigations of the effect of temperature on isotopic exchange have shown that the experimentally determined temperature dependence of the rate constants for thermal isotopic exchange corresponds to E_{obs} of the order of 56 kcal/mole. Hence E_{true} is about 5000 cal/mole. In reality it is 5500 cal/mole for the reaction $H_2 + D$, and about 4300 cal/mole for $H + D_2$.

For the complete dissociative scheme with formation of HD by recombination of H atoms with D atoms, the true activation energy $E_{true} = 0$, while the observed activation energy would coincide with the heat of dissociation of molecular hydrogen (~ 102 kcal/mole) i.e., it would exceed by about 45 kcal, the activation energy of semidissociative exchange. It is evident that such exchange could become predominant only in quite exceptional conditions.

The above reasoning is applicable to the homomolecular exchange of any A_2 molecules, and thermal isotopic exchange of other diatomic molecules should naturally be expected to follow the same course. This mechanism is applicable to the halogens. For oxygen $Q_{diss} = 118$, and therefore the dissociation component of the exchange activation energy $Q/2 \quad 59$ kcal/mole. The true activation energy of this process is unknown, but it is apparently not large, perhaps owing to the process $O_2 + O \rightarrow O_3 \rightarrow O_2 + O$.

In consequence, although the observed activation energies and rates are less than for hydrogen, the differences of the rates should not be large. For nitrogen, according to the most recent data, $Q_{diss} > 200$ kcal/mole. This gives for the energy which enters the relationship between the equilibrium N_2 concentrations and the temperature, $Q/2 > 100$ kcal, and therefore $E_{obs} \quad E_{true} + \frac{Q}{2} \gg 100$ kcal. At the usual temperatures of thermal reactions the N_2 concentrations and exchange rates should be immeasurably small.

The semidissociative mechanism appears in particularly pure form in the artificial formation of free atoms in a cold gas. An interesting example of such exchange was recently described for oxygen.

A mixture of O_2^{16} and O_2^{18} molecules (and some O_2^{17}) was irradiated by ultraviolet light, capable of inducing dissociation of oxygen into atoms [36]. Homomolecular isotopic exchange took place, leading to the formation of molecules of $O^{16}O^{18}$ (and also $O^{17}O^{16}$ and $O^{17}O^{18}$). The process takes the following course:

$$\left.\begin{array}{ll} 1. & O_2^{16} + h\nu = 2O^{16}, \\ & O_2^{18} + h\nu = 2O^{18}; \\ 2 & O_2^{18} + O^{16} = O^{18}O^{16} + O^{18}; \\ & O_2^{16} + O^{18} = O^{18}O^{16} + O^{16} \end{array}\right\} \qquad (34)$$

etc. The absolute concentrations of free O atoms are very low, and are constant at a constant light intensity. The aggregate equation may be written as

$$O_2^{16} + O_2^{18} \rightarrow 2O^{16}O^{18}. \qquad (34a)$$

Since in each elementary stage a free atom of another isotope is formed, the process constitutes a chain reaction The length of the chain is limited by recombination of atoms in the volume and at the walls, and also by the consumption of oxygen atoms for the oxidation of impurities, which are always present to some extent in the gas. Recombination with intermediate formation of ozone is also possible

$$\left.\begin{array}{l} a)\ O + O + O_2 \rightarrow 2O_2; \\ b)\ O + O + \text{wall} \rightarrow O_2 + \text{wall}; \\ c)\ O + O_2 + O_2 \rightarrow O_3 + O_2; \\ d)\ O_3 + O \rightarrow 2O_2. \end{array}\right\} \qquad (34b)$$

Consequently considerable variations of the chain length are to be expected according to the experimental conditions. In the conditions of Johnston and O'Shea's experiments the quantum yield was 125, and the chain length was of the same order.

Isotopic exchange of N_2^{14} with N_2^{15} molecules proceeds by an atomic mechanism in the electric discharge [37].

The above examples belong to the relatively small class of homomolecular isotopic exchange reactions between molecules of elements. However, the applicability of this mechanism is by no means confined to this class. As an example, we may note the results of a study of isotopic exchange between hydrogen chloride and molecular chlorine in the gas phase, carried out with the long-lived radioactive isotope Cl^{36}. In an early investigation [38] extremely rapid isotopic exchange was observed. It was found later [38a] that in the earlier work the catalytic effect of the vessel walls was not considered, and in reality a rapid heterogeneous process rather than a slow homogeneous one had been studied. If the walls of the glass vessel are coated with a mixture of saturated fluorocarbons of high molecular weight, it is possible to suppress heterogeneous exchange almost entirely. In these conditions photochemical exchange in visible light, absorbed by chlorine, can easily be studied. The authors used monochromatic light of wave length 3650 A. The mechanism of this exchange is probably atomic:

$$\left.\begin{array}{ll} & a)\ Cl_2 + h\nu = 2Cl; \\ & b)\ Cl + H\overset{*}{Cl} = HCl + \overset{*}{Cl}, \\ \text{and then either} & \\ & c)\ Cl_2 + \overset{*}{Cl} \rightarrow Cl\overset{*}{Cl} + Cl, \\ \text{or} & d)\ \overset{*}{Cl} + Cl \rightarrow Cl\overset{*}{Cl}. \end{array}\right\} \qquad (35)$$

The radiation intensity was measured by a chemical actinometer and thermopile. In 1 minute from $2.2 \cdot 10^{16}$ to $2.6 \cdot 10^{16}$ photons were absorbed in the reaction vessel in different experiments. This, in conjunction with the isotopic exchange rate, gave 110 for the quantum yield in the conditions used. It should be noted that the effect of treatment of the walls with organic fluorides on the half-exchange time implies the existence, never previously considered, of heterogeneous exchange between chlorine isotopes at the glass vessel surface.

Among other examples of semidissociative exchange we may mention the thermal isotopic exchange between iodine vapor and organic iodides in the gas phase, effected through iodine atoms:

$$\left.\begin{array}{c} I_2 \rightleftharpoons 2I; \\ I + R\overset{*}{I} \rightarrow RI + \overset{*}{I}; \\ \overset{*}{I} + I \rightleftharpoons I\overset{*}{I}. \end{array}\right\} \qquad (36)$$

In its simple classical form, the dissociative atomic mechanism in homogeneous exchange is found only in gases. Because of the high dissociation energies of most chemical bonds, this mechanism cannot play any significant role at room temperature and below. The temperatures for an equal degree of dissociation of different molecules are directly proportional to the dissociation energies of these molecules, for example, for nitrogen, oxygen, hydrogen, chlorine, and iodine the corresponding ratios are

$$T_{N_2} : T_{O_2} : T_{H_2} : T_{Cl_2} : T_{I_2} \cong D_{N_2} : D_{O_2} : D_{H_2} : D_{Cl_2} : D_{I_2} = \\ = (230) : 117 : 103 : 57 : 35.4^*$$

Even for iodine the degree of dissociation at 25°C is only $1.41 \cdot 10^{-11}$. For hydrogen the same degree of dissociation is reached at a temperature of $298° \cdot \frac{103}{35.4}$, i.e., at 891°K. Therefore, for gases, the homogeneous dissociation exchange mechanism is typical for high temperatures. The dissociation products are not charged This mechanism is assumed to be predominant also at low temperatures at solid surfaces.

In solutions the situation is totally different. Because of solvation effects, even the most stable bonds are easily broken, especially in polar solvents with high dielectric constants. The dissociation products are, in general, ionized. However, dissociation into neutral particles – atoms and radicals – is also possible in solution. In particular, molecular iodine dissociates appreciably into atoms in most solvents even at room temperature. The formation of "free" organic radicals in solutions is well known. The classic example is the dissociation of hexaphenylethane into two triphenylmethyl radicals containing trivalent carbon.

An example of isotopic exchange proceeding in solution by way of dissociation is provided by the exchange of metal cations in soluble salts. The classical first demonstration of this exchange was with bivalent lead salts.

---

*The value for D_{N_2} is doubtful. According to the most recent data, it is about 225 kcal/mole.

As long ago as 1920, Hevesy and Zechmeister [39] who crystallized, by cooling, lead acetate from aqueous solution with an equivalent content of lead formate tagged with a radioactive isotope, found equipartition of radioactivity to take place, undoubtedly as the result of the processes

$$\left.\begin{array}{l} \underset{\text{cryst.}}{\mathrm{Pb(C_2H_3O_2)_2}} \rightarrow \mathrm{Pb^{2+}} + \underset{\text{solution}}{\mathrm{2C_2H_3O_2^-}}, \\ \underset{\text{cryst.}}{\overset{*}{\mathrm{P}}\mathrm{b(CHO_2)_2}} \rightarrow \overset{*}{\mathrm{P}}\mathrm{b^{2+}} + \underset{\text{solution}}{\mathrm{2CHO_2^-}}, \\ \text{mixing } \overset{*}{\mathrm{P}}\mathrm{b^{2+}_{aq}} \text{ with } \mathrm{Pb^{2+}_{aq}}, \\ \underset{\text{solution}}{\overset{*}{\mathrm{P}}\mathrm{b^{2+}} + \mathrm{C_2H_3O_2^-}} \rightleftarrows \underset{\text{cryst.}}{\overset{*}{\mathrm{P}}\mathrm{b(C_2H_3O_2)_2}} \end{array}\right\} \qquad (37)$$

In view of the slowness of the method used, the authors were able to determine only the upper limit of the exchange rate ($t_{1/2} < 15$ min). The same authors also discovered exchange leading to equipartition of radioactivity in pyridine solutions containing $PbCl_2$ and $\overset{*}{P}b(NO_3)_2$.

By analogy, isotopic exchange of iodine between KI^{131} and BaI_2^{127}, of hydrogen between DCl and H_2SO_4, etc., should occur simultaneously in solutions.

It must be remembered that electrolytic dissociation in solution is far more complex than the dissociation of hydrogen or of iodine vapor into atoms. The solutions contain not free positive and negative ions, but their solvates, so that essentially the process is always dissociation with complex formation rather than simple dissociation. Such effects are still more prominent in isotopic exchange between central atoms of different complexes, central atoms and "free" cations, etc.. A.A. Grinberg and L.E. Nikolskaya [40] consider a dissociation mechanism probable for the exchange of $[PtI_4]^{2-}$ with $\overset{*}{I}^-$. American authors postulate an ionization mechanism for the isotopic exchange of tertiary butyl iodide with sodium iodide in liquid sulfur dioxide [41]

$$(CH_3)_3CI + Na\overset{*}{I} \rightarrow (CH_3)_3C\overset{*}{I} + NaI \qquad (38)$$

and for tertiary butyl chloride with lithium chloride in anhydrous formic acid [42].

The kinetic grounds adduced in favor of this do not appear to us entirely convincing. At the same time, as will be shown in the next section, a semidissociative mechanism is very typical for isotopic exchange between organic and inorganic halides; here the halide ions formed by salt dissociation and undissociated molecules of the organic halides take part in the exchange

$$RHal + \overset{*}{H}al^- \rightarrow R\overset{*}{H}al + Hal^-. \qquad (39)$$

An instructive example of the dissociation mechanism has recently been found in the isotopic exchange between bi- and univalent mercury ions in perchlorate solutions

$$Hg^+ + \overset{*}{H}g^{2+} \rightarrow Hg^{2+} + \overset{*}{H}g^+. \qquad (40)$$

As was first shown by Haissinsky and Cottin [43], this process is very rapid in acid solutions. This was confirmed by their later researches, in which various methods were used for separation of univalent and bivalent mercury. These were based on the low solubilities of a number of univalent mercury salts: Hg_2Cl_2, Hg_2SO_4, Hg_2CrO_4 etc. It is not desirable to leave Hg_2^{2+} ions in solution with precipitation of Hg^{2+}, because of the reversible dissociation of Hg_2^{2+}.

Formally, the reaction appears to be of the purely electronic type, but it does not conform to the general law that the exchange between simple ions by this mechanism is not very rapid. At the same time, Equation (40) represents the chemistry of the reaction incorrectly, as in reality the univalent mercury ion consists of the Hg_2 group carrying two positive charges (Hg_2^{2+}). Isotopic exchange between bi- and univalent mercury ions may be retarded by addition of CN^- ions. In such conditions the reaction kinetics can be investigated [44]. The results of experiments performed with Hg^{203}, in conjunction with literature data on the kinetics of the dismutation of the Hg_2^{2+} ion, which is an intracomplex oxidation–reduction reaction

$$(\overset{\ominus\curvearrowright}{Hg : Hg})^{2+} \longrightarrow Hg^{2+} + Hg, \qquad (41)$$

lead to the conclusion that the process is effected by means of heterolytic rupture of the Hg : Hg bond without division of the electron pair. Wolfgang and Dodson [44] have shown convincingly that rapid isotopic exchange in absence of ions is also effected by way of dismutation, consisting of dissociation into two unequal particles Hg^{2+} + Hg.

The process as a whole may be regarded as occurring on the basis of two very rapid and completely reversible reactions

$$\left.\begin{array}{l} \text{a)}\ Hg^{2+}_{2aq} \rightarrow Hg^{2+}_{aq} + Hg_{aq}, \\ \text{b)}\ \overset{*}{H}g^{2+}_{aq} + Hg_{aq} \rightarrow (\overset{*}{H}gHg)^{2+}_{aq}, \end{array}\right\} \qquad (42)$$

the result of which is the process (40), which we can write as

$$Hg_2^{2+} + \overset{*}{H}g^{2+} \rightarrow (\overset{*}{H}gHg)^{2+} + Hg^{2+} \qquad (43)$$

This example demonstrates the care which should be taken in classifying a reaction as belonging to a definite type. Additional examples of exchange by a dissociation mechanism in solutions are given in §9 of this chapter and in Chapter V.

§7. Dissociative Heterogeneous Exchange

There are heterogeneous analogs to the dissociative exchange reactions considered in the previous section. This category includes, for example, many instances of isotopic exchange of liquids and solids with their vapors (vaporization/condensation) or with saturated solutions (solution/crystallization). In such processes it is difficult to avoid complications caused by changes of degree of dispersion or of phase structure. For example, in the isotopic exchange of mercury droplets with mercury vapor the evaporation and condensation processes will be accompanied by assimilation of the smaller droplets, with higher free energy, by the larger, and ultimately this should lead to the conversion of a system of small droplets into one large drop. Such effects are still more prominent in solids which, in addition to crystallites of various sizes, may also contain defects with increased free energy, unstable face forms, etc. If such a solid is in contact with its own vapor or saturated solution, it is difficult to avoid the healing of defects and changes of crystal face forms and degree of dispersion, induced by the same mechanism of reversible transfer of atoms, molecules, and ions from the solid phase into the gas or liquid phase as that which forms the basis of such heterogeneous phase exchange. In the isotopic exchange of a metal with solutions of its ions further complications arise, associated with microchemical processes of the corrosion type, which increase in prominence with increasing numbers of inclusions with a different electrochemical potential in the metal surface.

Heterogeneous exchange by a dissociative physicochemical mechanism of evaporation or dissolution is closely related to isotopic exchange involving reversible chemical decomposition. For example, at temperatures at which appreciable reversible dissociation of oxides into lower oxides and oxygen, or into metals and oxygen, occurs, such chemical dissociation must inevitably lead to isotopic oxygen exchange, while at the dissociation temperatures of carbonates into oxides and carbon dioxide isotopic exchange of C and O is inevitable, etc.

§8. Association Mechanism

The association mechanism is very common in isotopic exchange reactions both in ionized and in nonionized solutions. It is found less frequently in isotopic exchange in gases and vapors. One of the simplest examples was discovered by us in 1934 in experiments with radioactive halogens [45]. Gaseous bromine was blown through potassium bromide solution containing radioactive bromine isotope Br^{82}. Isotopic exchange occurred practically instantaneously. The following mechanism was then postulated for the exchange. A negative bromide ion and a bromine molecule form a negatively charged Br_3^- ion. Polyhalogen ions of this type are well known in the case of bromine and iodine. The three halogen atoms in them are probably identical, forming an equilateral triangle. The exchange scheme would not change substantially with a different structure of the complex (for example, $Br^- Br_2$). Decomposition of the Br_3^- complex can occur with the rupture of any of the three equivalent bonds, with the excess electron at any one of the bromine atoms. The bromine molecule remains neutral

$$\left.\begin{array}{l}\overset{*}{Br}{}^- + Br_2 \rightarrow (\overset{*}{Br}BrBr)^-;\\ (\overset{*}{Br}\cdot BrBr)^- \rightarrow \overset{*}{Br}Br + Br^-.\end{array}\right\} \qquad (44)$$

Depending on the point of rupture in the Br_3^- ion, the simple Br^- ion can consist of the atom either of the radioactive or of the inactive isotope. If such decompositions occur sufficiently frequently, following the laws of chance to the accuracy of the isotopic corrections, equipartition of the radioactive isotope between the bromine ions and molecules should be established.

The association mechanism of halogen exchange can now be regarded as generally accepted. Isotopic exchange of oxygen between water and carbon dioxide, isotopic exchange of hydrogen between ammonia and water, etc., proceed similarly.

$$\left.\begin{array}{l}CO_2^{16} + H_2O^{18} \rightleftarrows H_2CO_2^{16}O^{18} \rightleftarrows H_2O^{16} + CO^{16}O^{18};\\ ND_3 + H_2O \rightleftarrows [ND_3H]^+OH^- \rightleftarrows ND_2H + DHO.\end{array}\right\} \qquad (45)$$

Associative exchange is based on a combination of the following processes: a) formation of associated complexes, and b) their decomposition. The content of such complexes in a system at any instant is close to equilibrium; and in some cases can be calculated quantitatively. The rate R of the process is determined both by the equilibrium content of the complexes and by the rate of their decomposition.

The complexes which appear in Equations (44) and (45) have a relatively long life and are quite definite although unstable chemical forms. Exchange with the intermediate formation of extremely unstable intermediate complexes which exist only for the duration of the collision is very common. A very important role is attributed to such complexes in modern kinetics [8, 46].

§ 9. Associative Exchange with Formation of Intermediate Complexes Only

The isotopic exchange of halogens of organic molecules with halide ions in aqueous and alcoholic solutions

$$R_1Hal + \overset{*}{Hal}{}^- \rightarrow R_1\overset{*}{Hal} + Hal^-. \qquad (46)$$

has been extensively studied. In cases when the organic molecule is optically active, isotopic exchange is accompanied by change in the sign of rotation of the plane of polarization. Such changes of rotation were known previously in the replacement of halogens by each other in organic molecules, and they are special cases of the Walden inversion [47] (see also § 20 of this chapter).

By means of the tetrahedral space model of the carbon atom it can be shown that the Walden inversion corresponds to a "reversal" of the carbon tetrahedron. According to Polanyi, this occurs in two stages. First the substituent group attaches itself to the organic molecule from the side opposite to the location of the exchanging atom, forming an intermediate complex. This structure of the intermediate complex is advantageous if the exchanging atom is charged and the other atoms and groups are neutral, as the further apart two similarly charged ions which replace one another are [8], the less is their mutual repulsion (this is discussed in greater detail in § 20 of this chapter). The intermediate complex, i.e., the quasi-molecule which represents successfully oriented molecules at the moment of collision, exists for about $10^{-10}-10^{-12}$ second, and then decomposes again. The decomposition products may be the original molecule and the original exchanging atom (or ion). In such case no "reversal" of the tetrahedron or optical inversion takes place. The second possibility is the ejection, in the form of an ion, of an atom which formerly was part of the molecule, and its replacement in the latter by an atom of the substituent ion. The molecule so formed should have a new spatial configuration (Fig. 46). The occurrence of Walden inversion in isotopic exchange is convincing proof of associative mechanism of substitution of the type described. It must be stressed that, strictly speaking, a combination of a dissociative and an associative mechanism is involved in this instance, but only the second is explicitly considered in view of the rapidity and reversibility of the second [47]. Isotopic exchange with tetrahedron reversal is characterized by the fact that the isotopic exchange rate and the racemization rate coincide.

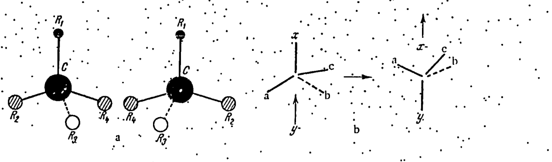


Fig. 46. a) Structure of two optical antipodes of asymmetric molecules, b) isotopic substitution with tetrahedron reversal (Walden inversion). Bonds directed under the plane of the diagram are shown as broken lines.

§ 10. Exchange with Transfer of Isotopes within Radicals, Molecules, and Polyatomic Ions

The preceding sections included numerous examples of isotopic exchange effected by transfer of electrons, atoms, and simple monoatomic ions.

As has already been noted, the transfer of a given isotope from one substance to another may be the consequence of transfer of more complex particles such as di- and polyatomic ions, neutral radicals, and molecules. In such cases the isotopic exchange rate represents not the chemical mobility of the atom which appears in the stoichiometric equation for the exchange, but the mobility of the more complex particle containing the particular isotope. A correct understanding of the type of particle transferred in the exchange (electrons, atoms, simple ions, polyatomic ions, radicals, or molecules) is very important for an understanding of the exchange mechanism and correct theoretical interpretation of it. Unfortunately, the nature of the particles transferred is often difficult to establish.

We shall now consider some examples of isotopic exchange involving the transfer of particles consisting of two or more atoms.

Observations indicating the possibility of slow exchange of solvate layers of molecules with each other and with the solvent were already made a long time ago in our association in the course of work with radioactive bromine isotopes [45]. The results of these early investigations were disputed [48] and the question remained incompletely settled owing to the war, which prevented the completion of the difficult confirmatory investigations which had been started. It was later shown in a study of the distribution of heavy oxygen between dissolved hexahydrates of trivalent metal salts – chromium, aluminum, and others – that in all cases oxygen from the water of the hydrated cation $[Me(H_2O)_6]$ passes into the solvent, water, and in some systems the rate of this transfer is so low that it can easily be determined. The most complete investigations were performed by Taube et al. [49], at room temperature in acid perchlorate solutions. Oxygen is exchanged more slowly by chromium salts than by others. For example, in one experiment, at 25°C in a solution of perchlorate in water tagged with O^{18} and containing $Cr(ClO_4)_3 \cdot 6H_2O$ (1.47 M) + $HClO_4$ (0.13 M), the half-equilibrium time for Reaction (47) was 40 hours.

$$[Cr(H_2O_{16})_6{}^{3+} + H_2O^{18} \rightarrow [Cr(H_2O^{16})_5(H_2O^{18})]^{3+} + H_2O^{16}. \qquad (47)$$

Distribution of O^{18} between salt and solvent was determined by isotope analysis of small portions of water which had been distilled off. In these conditions exchange of O^{18} and O^{16} between H_2O and ClO_4^- is much slower than exchange according to Equation (47), and it may be completely ignored [49].

In contrast to this, in strongly acid perchlorate solution of trivalent cobalt hexahydrate, complete exchange is reached in 2 minutes by a reaction analogous to (47). Very rapid exchange was found for ferric iron and bivalent cobalt hexahydrates. In all these cases dissociation of water into $2H^+$ and O^{2-} is completely excluded, while dissociation into H^+ and OH^- is negligible because of the shift of equilibrium induced by the presence of a strong acid in considerable concentration. Therefore exchange by way of previous dissociation of the water of the hydrated cation and solvent with subsequent recombination may be regarded as excluded, and the combination of indirect data is convincingly in favor of exchange by whole water molecules carrying O^{18}.

A similar mechanism has been established for isotopic exchange of carbon and nitrogen between cyanide complexes of many metals and free cyanide ions [1].

This reaction type is similar in mechanism to isotopic exchange effected by group transfer in ordinary chemical reactions. Typical examples are the isotopic exchange of carbon between gaseous CO_2 and $HCO^-_{3\,sol}$ and exchange of nitrogen between NO and NO_2 or of sulfur between SO_2 and $H_2SO_{3\,sol}$.

The first of these reactions, which has been studied by many authors, is discussed in detail in A.I. Brodsky's monograph [50]. The exchange between carbon dioxide tagged with heavy inactive carbon isotope and a dissolved alkali metal bicarbonate is represented by the aggregate equation

$$C^{13}O_2 + HC^{12}O_3^- = C^{12}O_2 + HC^{13}O_3^-. \tag{48}$$

This proceeds by hydration and dehydration

$$\left.\begin{aligned} &a)\ C^{13}O_2 + H_2O \rightarrow HC^{13}O_3^- + H^+;\\ &b)\ HC^{12}O_3^- \rightarrow H_2O + C^{12}O_2. \end{aligned}\right\} \tag{49}$$

Both processes in (49) are reversible. Their joint occurrence in the directions represented by stages "a" and "b" leads to isotopic exchange.

The mechanism represented by Equations (49) is probably similar to the mechanism of isotopic exchange between barium carbonate, used for radioactive carbon radiometry, and atmospheric carbon dioxide. This exchange, which proceeds at an appreciable rate in moist air, often leads to errors in tracer studies with C^{14}. The aggregate exchange equation may be written:

$$BaC^{14}O_3 + CO_2^{12} \rightarrow BaC^{12}O_3 + C^{14}O_2. \tag{50}$$

The accelerating effect of water is probably due to the formation of more rapidly exchanging acid carbonates $Ba(HCO_3)_2^-$. The radioactive carbon leaves the solid carbonate and goes into the atmosphere in the form of $C^{14}O_2$.

The mechanism of isotopic exchange between nitrogen oxides is also well established. In a gaseous mixture consisting of $N^{14}O$ and $N^{15}O_2$, very rapid redistribution of nitrogen occurs; according to the equation

$$N^{14}O + N^{15}O_2 \rightarrow N^{15}O + N^{14}O_2. \tag{51}$$

The process is effected without intermediate separation of nitrogen atoms [51], by an association mechanism

$$\left.\begin{aligned} &N^{14}O + N^{15}O_2 \rightarrow N^{14}N^{15}O_3;\\ &N^{14}N^{15}O_3 \rightarrow N^{15}O + N^{14}O_2. \end{aligned}\right\} \tag{52}$$

As is known, N_2O_3 has the symmetrical structure $O = N - O - N = O$, and therefore in dissociation, which is an internal oxidation–reduction process, both regeneration of the original $N^{14}O$ and $N^{15}O_2$ molecules, and formation of the isotopic exchange products $N^{15}O$ and $N^{14}O_2$, are equally probable. We have shown only the second of these reactions, which leads to isotopic exchange. The stages in the exchange of nitrogen between its two oxides according to Equation (52) are analogous to the stages in the exchange of bromine between Br^- and Br_2 according to Equation (44). The principal distinction lies in the nature of the transferred particles. In the case of bromine, these are atoms and simple atomic ions, so that isotopic exchange in pure form occurs; in the case of nitrogen, NO and NO_2 molecules are transferred and the transfer of these radical molecules is accompanied by isotopic exchange of nitrogen.

In all the examples discussed above the transferred molecules or radicals are not large. An interesting example of isotopic exchange by much larger radicals was recently described in the papers by I.N. Guryanova and V.N. Vasilyeva [52], mentioned in Chapter II. It was found in a study of the exchange of sulfur isotopes between organic di- and polysulfides and thiols that sulfur is transferred in the form of the corresponding sulfide radicals. For example, in the isotopic exchange of diparatolyl disulfide with thiocresol, $p\text{-}CH_3C_6H_4S$ radicals are transferred, which are formed by dissociation both of the disulfides and of the thiols:

$$\left.\begin{aligned} &(p\text{-}CH_3C_6H_4)_2\overset{*}{S}S \rightleftarrows p\text{-}CH_3C_6H_4\overset{*}{S} + p\text{-}CH_3C_6H_4S;\\ &p\text{-}CH_3C_6H_4SH \rightleftarrows p\text{-}CH_3C_6H_4S + H. \end{aligned}\right\} \tag{53}$$

Although the detailed mechanism is not entirely clear and, in particular, it is not known whether the dissociation products are neutral or charged, the transfer of sulfur within large organic radicals is proved conclusively by studies of the exchange of sulfur between different disulfides and between disulfides and thiols containing different radicals in the molecules.

§ 11. Isotopic Exchange as the Result of an Elementary Chemical Reaction

In some of the examples which have been considered, isotopic exchange was the consequence of concealed elementary chemical reactions in a state of dynamic equilibrium. This mechanism is very common, and is convincingly demonstrated by the following examples.

1. According to Ogg, rapid exchange of nitrogen between NO_2 and N_2O_5 takes place in the gas phase and in inert solvents. The kinetics of this reaction was studied with the aid of radioactive nitrogen N^{13} and heavy nitrogen N^{15}, and compared with the kinetics of monomolecular decomposition of N_2O_5 [51]. As a result, it was established with a high degree of probability that the exchange takes place by way of reversible thermal decomposition of the pentoxide into NO_2 and NO_3. By combining with NO_2 molecules of a different isotopic composition, NO_3 yields tagged nitrogen pentoxide. Consequently, the exchange occurs with the aid of NO_2 molecular radicals.

2. The work of Soviet scientists has shown [53] that alcohols in presence of a number of oxides are good hydrogenating agents, which are converted into aldehydes during the hydrogenation. The following reaction occurs in mixtures of C_2H_5OH with aldehydes containing any number of carbon atoms:

$$C_2H_5OH + C_nH_{2n}O \rightarrow C_2H_4O + C_nH_{2n+1}OH. \tag{54}$$

Both saturated and unsaturated aldehydes can be converted into alcohols by hydrogen from ethanol. If the number of carbon atoms in the alcohol and the aldehyde molecules is the same, and the same radical is linked to $-CH_2OH$ in the one and to $-CHO$ in the other, then the only consequence of reduction of the aldehyde and oxidation of the alcohol is invisible exchange of hydrogen atoms

$$\overset{*}{R}_1CH_2OH + R_1CHO \rightarrow \overset{*}{R}_1CHO + R_1CH_2OH. \tag{55}$$

A tangible result is obtained with different isotopic compositions of the carbon in the original alcohol and aldehyde. If the aldehyde contains radioactive carbon and the alcohol does not, the transfer of two H atoms from the alcohol molecule to the aldehyde molecule leads to a decrease in the radioactive carbon content of the aldehyde and its appearance in the alcohol, i.e., to isotopic exchange

$$\left.\begin{aligned} &CH_3CH_2OH + C^{14}H_3CHO \rightarrow CH_3CHO + C^{14}H_3CH_2OH,\\ &CH_3CH_2OH + CH_3C^{14}HO \rightarrow CH_3CHO + CH_3C^{14}H_2OH \end{aligned}\right\} \tag{56}$$

Here the structural position of C^{14} at the α- or β-carbon atom is retained, and exchange between the aldehyde and alcohol does not result in exchange between the CH_3 group and the CH_2OH group of the alcohol, or the CH_3 group and the CHO aldehyde group. Hydrogen is transferred from one molecule to another, and this leads to isotopic exchange of carbon. This type of isotopic exchange in presence of oxides of aluminum and zinc has been recently studied by O.M. Vinogradova and N.P. Keier [53a].

3. For our third example we shall consider the exchange of sulfur and oxygen between sulfur dioxide and sulfur trioxide. In presence of a catalyst the dynamic equilibrium $2SO_3 \rightleftharpoons 2SO_2 + O_2$ is established very rapidly, and in consequence both the sulfur and the oxygen isotopic compositions of the two oxides should become identical.

4. Interesting types of isotopic exchange were discovered in the course of investigations of the catalytic cracking of hydrocarbons with the use of molecules tagged with radioactive carbon.

In mixtures of tagged olefins ($C^{14}C^{12}H_4$ or $C^{14}C_2^{12}H_6$ etc.) with paraffins, passed over aluminosilicate cracking catalysts at 400°C and over, some of the radioactive carbon passes into the paraffins; this can only be explained by destructive alkylation according to the equation.

$$C^{12}H_2C^{14}H_2 + \text{iso-}C_8^{12}H_{18} \rightarrow C^{12}H_2C^{12}H_2 + \text{iso-}C^{14}C_7^{12}H_{18}. \qquad (57)$$

Without considering in detail the alkylation mechanism, which most probably proceeds by way of carbonium ions, we will note that analogous reactions of ethylene, accompanied by increase of the olefin molecule, are known, up to the reaction

$$C_2H_4 + C_nH_{2n+2} \rightarrow C_3H_6 + C_{n-1}H_{2n}. \qquad (58)$$

In the case of propylene and higher olefins, reactions are known which lead to an increase of the olefin molecule and a decrease of the paraffin molecule, as well as reactions in which the number of carbon atoms in the olefin molecule decreases, and that in the paraffin molecule increases

$$\left.\begin{array}{l} C_3H_6 + C_nH_{2n+2} \rightarrow C_4H_8 + C_{n-1}H_{2n}, \\ C_3H_6 + C_nH_{2n+2} \rightarrow C_2H_4 + C_{n+1}H_{2n+4} \end{array}\right\} \qquad (58a)$$

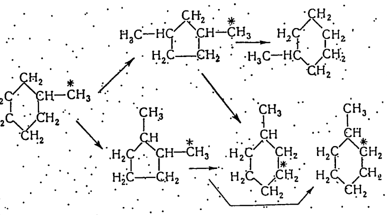
etc.

All these are examples of destructive alkylation, easily effected in presence of a number of catalysts. Reaction (57) and similar reactions cannot be detected by the usual methods, since their only result is a different distribution of the C^{14} isotope between the molecules. There is no doubt that it belongs to the category of isotopic exchange reactions.

A still more curious example is that discovered by M.M. Sakharov [57] for methylcyclohexane. If methylcyclohexane tagged in the methyl group is brought into contact with aluminosilicate catalysts at the appropriate temperatures, part of the radioactivity passes into the hexamethylene ring. From a study of the ordinary chemical reactions of methylcyclohexane under the same conditions it appears highly probable that this conversion, which is a peculiar form of intramolecular isotopic exchange

$$C_6H_{11}\overset{*}{C}H_3 \rightarrow C_5\overset{*}{C}H_{11}CH_3, \qquad (59)$$

is based on reversible conversions into rings with different numbers of atoms, in the first instance five, possibly according to the scheme


(59a)

etc. Unfortunately, the relative contents of methylcyclohexanes tagged in the ring at the para-, meta-, and ortho-positions relative to the methyl group have not yet been investigated.

The above examples illustrate the frequent occurrence of isotopic exchange caused by transfer of particles consisting of two or more atoms, and the presence among these processes of all the types met in exchange with transfer of atoms and monoatomic ions.

§ 12. Complete Stage Scheme of Isotopic Exchange

In our discussion of different isotopic exchange mechanisms, the dissociation and association mechanisms were sharply contrasted for the sake of greater clarity. In reality, the distinction between these mechanisms is to a considerable extent conventional. In both cases isotopic exchange includes dissociation and association stages, and the distinction between them is based on the sequence of the stages: in the dissociation mechanism the original molecules are first dissociated and this is followed by association of the dissociation products into new particles, while in the association mechanism the original particles first combine (associate) into larger ones, and these dissociate into different new particles. Often the intermediate exchange products in one and the same reaction contain both parts of the original molecules, and molecules larger than the original molecules.

The distinction is even less sharp in isotopic exchange reactions in solutions. In such a case the dissociation itself occurs with the participation of the solvent molecules, and is essentially solvolysis, or a peculiar type of exchange reaction. For example, the very common dissociation of acids in water into protons and anions, which plays an important role in exchange, is hydrolysis with formation of hydronium ions and hydrated anions. Therefore dissociation in aqueous solutions should be represented as

$$AH_{aq} + H_2O \rightleftharpoons H_3O^+ + A^-_{aq} \qquad (60)$$

More generally, according to Brönsted, all acid and base dissociation and association processes are metathetical reactions [35]; for example, the dissociation of water into H^+ and OH^- ions should be represented as

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-, \qquad (61)$$

and not

$$H_2O \rightleftharpoons H^+ + OH^-.$$

The ionization of hydrogen fluoride and ammonia can be represented similarly

$$\left.\begin{array}{l} HF + HF \rightleftharpoons H_2F^+ + F^- \\ \text{and} \quad NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^- \end{array}\right\} \qquad (62)$$

In its turn, the reaction between an acid and a base is neither simple combination of the original molecules, nor simple recombination of H^+ and OH^- ions, but a metathetical reaction. For example, hydrogen chloride and ammonia in aqueous solution react, not according to the equations

$$\left.\begin{array}{l} NH_3 + HCl \rightleftharpoons NH_4Cl, \\ NH_4Cl \rightleftharpoons NH_4^+ + Cl^-, \end{array}\right\} \qquad (63)$$

but according to the scheme

$$\left.\begin{array}{l} NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-, \\ HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-, \\ H_3O^+ + OH^- \rightleftharpoons 2H_2O. \end{array}\right\} \qquad (64)$$

In these schemes the participation of the solvent molecules is not shown fully, as both H_3O^+ and Cl^- are surrounded by unstable hydrate layers. For the same reason it is difficult to draw a line between dissociation and association mechanisms in solutions. This may be illustrated by the following examples: A A. Grinberg et al. [40] made a detailed study of the isotopic exchange of complex anions of the type MeHal_4^{2-} with Hal^-, and of analogous complex cyanides with CN^- ions in aqueous solutions. In all cases, in addition to the dissociation mechanism which proceeds, according to the extent of the exchange, through the formation of MeHal_3^-, MeHal_2, MeHal^+ and, finally, Me^{2+} followed by re-association into MeHal_4^{2-}, but with different isotopic compositions of the Hal^- or CN^- ions respectively, an associative mechanism is also possible, whereby the MeX_4^{2-} group first adds on one or two H_2O molecules which enter the inner sphere of the complex, to form an intermediate associated activation complex $[\text{MeX}_4 \cdot H_2O]^{2-}$ or $[\text{MeX}_4 \cdot (H_2O)_2]^{2-}$. The first of these would have the nature of an intermediate collision complex, while the second could have greater stability. In both cases, association of the halide (or cyanide) and water into such complexes would be followed by dissociation with a new distribution of Hal^- and H_2O between the solution and the complex. This could be followed by two additional stages with participation of tagged Hal^- ions. As a concrete example, we shall write the equations for these stages with $[\text{HgI}_4]^{2-}$ and $\overset{*}{\text{I}}{}^-$ ions, with intermediate addition of one water molecule.

$$\left.\begin{array}{l} [\text{HgI}_4]^{2-} + H_2O \rightarrow [\text{HgI}_4 \cdot H_2O]^{2-}; \\ [\text{HgI}_4 \cdot (H_2O)]^{2-} \rightarrow [\text{HgI}_3 \cdot H_2O]^- + \text{I}^-; \\ [\text{HgI}_3(H_2O)]^- + \overset{*}{\text{I}} \rightarrow [\text{HgI}_3\overset{*}{\text{I}}(H_2O)]^{2-}; \\ [\text{HgI}_3\overset{*}{\text{I}}(H_2O)]^{2-} \rightarrow [\text{HgI}_3\overset{*}{\text{I}}]^{2-} + H_2O \end{array}\right\} \qquad (65)$$

According to A.I. Brodsky [56], two types of exchanging mechanism are possible for the exchange of deuterium between an organic molecule RH and DA, where RH may be a hydrocarbon, alcohol, organic amine, etc., while DA may be an inorganic or organic deutero acid, heavy water, heavy ammonia, etc.: 1) an ionization mechanism, comprising reversible transfer of protons and deuterons with intermediate formation of ions, and 2) a simple association mechanism. For example, for the exchange of hydrogen of acetylene with deuterium of heavy water, the following three mechanisms could in principle be postulated; the first two are ionization mechanisms, equivalent to the dissociation mechanisms discussed earlier, and the third is a purely associative mechanism.

$$\left.\begin{array}{l} C_2H_2 + HDO \rightarrow [C_2H_2D]^+ + OH^- \rightarrow C_2HD + H_2O; \\ C_2H_2 + HDO \rightarrow C_2H^- + [HDHO]^+ \rightarrow C_2HD + H_2O; \\ C_2H_2 + DHO \rightarrow HC\equiv CH \cdot DHO \rightarrow C_2HD + H_2O \end{array}\right\} \qquad (66)$$

or, in general form:

$$\left.\begin{array}{l} \text{a) } \overset{\curvearrowleft}{RH + DA} = RHD^+ + A^- \longrightarrow RD + HA; \\ \text{b) } \overset{\curvearrowright}{RH + DA} = R^- + HDA^+ \longrightarrow RD + HA; \\ \text{c) } RH + DA = RH \cdots DA \rightarrow RD + HA. \end{array}\right\} \qquad (67)$$

It should be noted that neither of the ionization mechanisms is purely dissociative, since intermediate formation of A^- or R^- ions is accompanied by the simultaneous appearance of associated RHD^+ or $[HDA]^+$ ions respectively. To which of the two molecules the hydrogen will pass in the form of a proton or deuteron, and which of the groups, R or A, will be formed as the dissociation product of the anion, depends on the relative strengths of RH and HA as proton acids. In the particular case of acetylene the second alternative will predominate, as C_2H_2 has clearly-defined acid properties. It should also be noted that intermediate stages have been omitted from the above scheme for the ionization exchange mechanism. In reality, as a general rule, an associated intermediate complex (RHDA) should always be formed, which decomposes into RHD^+ and A^- or into R^- and HDA^+ respectively. The second stage of the transition to RD + HA probably passes through the intermediate complexes $[(DRH)^+ \cdot A^-]$ or $[(HAD)^+ \cdot R^-]$, which decompose into RD and HA. In other words, the contradistinction between dissociation and association mechanisms is conventional not only for solutions in general, but also for the concrete example discussed. As a rule, combined association–dissociation mechanisms operate, with intermediate formation of the ions.

§ 13. Electronic Types of Isotopic Exchange Reactions

Despite the diversity of isotopic exchange mechanisms, their studies have revealed certain general relationships between isotopic exchange and the chemical structure of the exchanging compounds. They have been clearly established for the most thoroughly studied reaction of hydrogen exchange, but their applicability extends much further.

Sections 1, 2, and 3 contained detailed discussions of extreme examples of oxidation-reduction reactions which reduce to complete electron transfer between particles:

$$\overset{\overset{\ominus}{\curvearrowright}}{A + B} \longrightarrow A^+ + B^- \qquad (68)$$

Much more common are processes of the homolytic type, in which electron pairs of covalent chemical bonds are separated with formation of unsaturated mono- (R– or biradicals (–R–). If an unpaired electron is denoted by a dot, a monoradical can be written as $R\cdot$ and a biradical as $\cdot R\cdot$. Examples are: a) formation of two methyls from ethane; b) formation of H atoms and $\cdot SH$ from hydrogen sulfide; c) formation of the biradical $\cdot C_3H_6\cdot$ from trimethylene; d) formation of $\cdot C_2H_4\cdot$ from ethylene.

1. Formation of monoradicals from stable molecules:

$$\left.\begin{array}{l} H_3C:CH_3 \rightarrow H_3C\cdot + \cdot CH_3 \\ H:S:H \rightarrow \cdot HS + \cdot H \end{array}\right\} \qquad (69)$$

2. Formation of biradicals from stable molecules:

$$\left.\begin{array}{l} \quad :CH_2: \\ CH_2:CH_2 \rightarrow \cdot CH_2:CH_2:CH_2\cdot \\ H_2C::CH_2 \rightarrow \cdot CH_2:CH_2\cdot \end{array}\right\} \qquad (70)$$

To each process of single bond dissociation with the appearance of two unpaired electrons there corresponds its own recombination process. In addition, owing to the high reactivity of unpaired electrons, free radicals and atoms are capable of adding on radicals and atoms contained in saturated molecules. The original free radicals and atoms then disappear, and, because of the separation of the electron pairs in the original saturated molecules, new unsaturated particles are simultaneously formed. Examples are the reactions of hydroxyl, methyl, and ethylene biradical, shown in the following equations:

1. Reaction of monoradical substitution:

$$\left.\begin{array}{l} \cdot OH + H:CH_3 \rightarrow H_2O + \cdot CH_3 \\ \cdot CH_3 + C_2H_5:NH_2 \rightarrow C_3H_8 + \cdot NH_2 \end{array}\right\} \qquad (71)$$

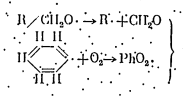
2. Reaction of biradical substitution:

$$\cdot CH_2 - CH_2\cdot + Cl:Cl \rightarrow \cdot C_2H_4 - Cl + Cl\cdot \qquad (71a)$$

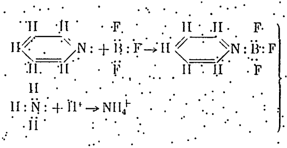
Purely electronic processes of reduction and oxidation of free atoms and radicals also occur easily, for example, the conversion of the OH radical in solution into a stable ion by the addition of an electron:

$$\overset{\overset{\ominus}{\curvearrowright}}{Fe^{2+} + \cdot OH} \longrightarrow Fe^{3+} + OH^- \qquad (72)$$

and, finally, the decomposition of large radicals into radicals and saturated molecules and addition of saturated molecules to radicals


(73)

Reactions of the third, acceptor–donor ("heterolytic") type are very common. In such a reaction, in the simplest case, hydrogen ions or neutral and charged particles, the electron shells of which are deficient in one pair of the neon or argon electron octet, become attached to free electron pairs of atoms of some other particles. Typical examples are provided by compounds of pyridine with boron fluoride and ammonia with protons through the free pair of the nitrogen atom

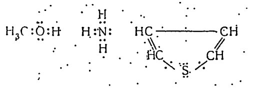

(74)

These addition reactions have their counterparts in the reverse reactions of heterolysis into neutral or charged particles with an incomplete number of electron pairs in the shell of one of the atoms. Various acceptor–donor substitution and metathetical reactions are still more common. The two most important groups of reactions of this type are proton transfers, forming the basis of the Bronsted protolytic mechanism for acid–base reactions, and processes of carbonium ion formation and conversion

$$\left.\begin{array}{l} C_2H_5OH + HCl \rightleftarrows C_2H_5OH_2^+ + Cl^- \\ C_2H_4 + H_2SO_4 \rightarrow C_2H_5^+ + HSO_4^- . \end{array}\right\} \qquad (75)$$

Between these three extreme types of reactions, which proceed: 1) with direct transfer of electrons between particles, 2) with splitting of electron pairs; and 3) with addition and separation without splitting of electron pairs, there are intermediate types with less definite electron displacements. This is in consequence of the peculiarities of the motion of electrons, which change their positions in space so rapidly that in quantum mechanics (the laws of which govern electronic processes) it is preferred to consider probabilities of electrons being in particular positions, rather than instantaneously changing positions. Such a probability may be quantitatively expressed in terms of electron cloud density (Fig. 47). This depends on the positions and the magnitude of the charges of the atomic nuclei, the type and degree of completeness of the electron shell containing the given electron, its energy, etc. It is shown by theory and experiment that electrons are always "spread"; and that the three types of electronic reactions considered above are merely limiting cases of less abrupt changes of the form and density of such clouds.

It was long ago shown experimentally that isotopic hydrogen exchange is greatly facilitated if atoms in one of the exchanging molecules have free electron pairs while the electron shells of the other exchanging molecules are deficient in such pairs. For example, compounds of oxygen, nitrogen, and sulfur contain available electron pairs, shown below for methyl alcohol, ammonia, and thiophene:



On the other hand, the electron shell of the central atom in trivalent boron and trivalent aluminum compounds,

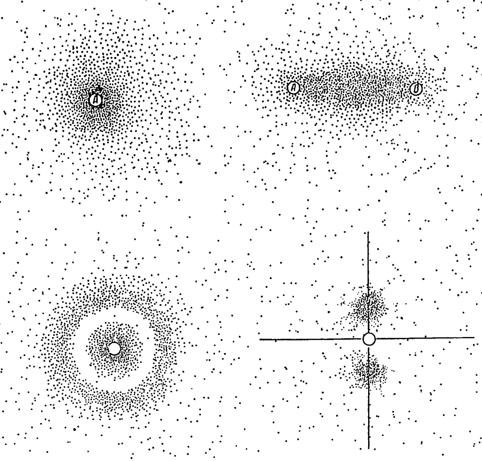
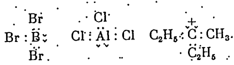


Fig. 47. Electron "cloud" in atoms and molecules, after Farkas. a) Schematic representation of a "cloud" corresponding to the 1s orbit in atom A; b) schematic representation of an electron "cloud" corresponding to a simple covalent s,s bond, c) schematic representation of an electron "cloud" corresponding to the 2s orbit; d) schematic representation of an electron "cloud" corresponding to the 2py orbit about the atomic nucleus A.

or of trivalent carbon in carbonium ions, is one electron pair short* of the number required to complete the electron shell of the nearest heavier inert gas



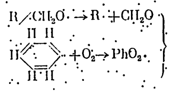
$$\begin{array}{c} Br \\ Br:\ddot{B}\check{\ } \\ \ddot{B}r \end{array} \qquad \begin{array}{c} Cl \\ Cl:\ddot{Al}:Cl \\ \check{\ }\check{\ } \end{array} \qquad \begin{array}{c} + \\ C_2H_5:\ddot{C}:CH_3 \\ \ddot{C}_2H_5 \end{array}$$

Each hydrogen ion is capable of adding on one electron pair. Quite often metal cations such as Hg^{2+}, Fe^{3+}, Ni^{2+} in solution behave as atoms, capable of participating as acceptors in the formation of several electron pairs. However, in such cases the energy of electrostatic attraction of oppositely charged or easily polarized particles plays an important role, while the acceptor–donor mechanism may be subordinated to it.

Numerous Soviet and foreign investigations have shown that hydrogen linked to oxygen, sulfur, or nitrogen enters isotopic exchange much more easily than hydrogen linked directly to carbon [56-58]. The electron shell

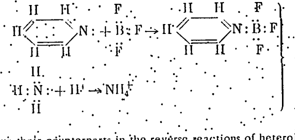
---

*Electron pair deficiency will be denoted by ˇˇ.



(73)

Reactions of the third, acceptor–donor ("heterolytic") type are very common. In such a reaction, in the simplest case, hydrogen ions or neutral and charged particles, the electron shells of which are deficient in one pair of the neon or argon electron octet, become attached to free-electron pairs of atoms of some other particles. Typical examples are provided by compounds of pyridine with boron fluoride and ammonia with protons through the free pair of the nitrogen atom



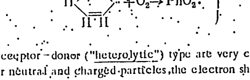
(74)

These addition reactions have their counterparts in the reverse reactions of heterolysis into neutral or charged particles with an incomplete number of electron pairs in the shell of one of the atoms. Various acceptor–donor substitution and metathetical reactions are still more common. The two most important groups of reactions of this type are proton transfers, forming the basis of the Bronsted protolytic mechanism for acid–base reactions, and processes of carbonium ion formation and conversion

$$\left.\begin{array}{l} C_2H_5OH + HCl \rightleftarrows C_2H_5OH_2^+ + Cl^- \\ C_2H_4 + H_2SO_4 \rightarrow C_2H_5^+ + HSO_4^- \end{array}\right\} \qquad (75)$$

Between these three extreme types of reactions, which proceed: 1) with direct transfer of electrons between particles, 2) with splitting of electron pairs; and 3) with addition and separation without splitting of electron pairs, there are intermediate types with less definite electron displacements. This is in consequence of the peculiarities of the motion of electrons, which change their positions in space so rapidly that in quantum mechanics (the laws of which govern electronic processes) it is preferred to consider probabilities of electrons being in particular positions, rather than instantaneously changing positions. Such a probability may be quantitatively expressed in terms of electron cloud density (Fig. 47). This depends on the positions and the magnitude of the charges of the atomic nuclei, the type and degree of completeness of the electron shell containing the given electron, its energy, etc. It is shown by theory and experiment that electrons are always "spread", and that the three types of electronic reactions considered above are merely limiting cases of less abrupt changes of the form and density of such clouds.

It was long ago shown experimentally that isotopic hydrogen exchange is greatly facilitated if atoms in one of the exchanging molecules have free electron pairs while the electron shells of the other exchanging molecules are deficient in such pairs. For example, compounds of oxygen, nitrogen, and sulfur contain available electron pairs, shown below for methyl alcohol, ammonia, and thiophene:



On the other hand, the electron shell of the central atom in trivalent boron and trivalent aluminum compounds,

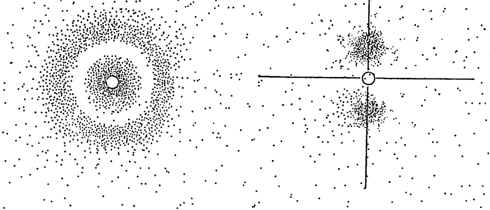


Fig. 47. Electron "cloud" in atoms and molecules, after Farkas. a) Schematic representation of a "cloud" corresponding to the 1s orbit in atom A; b) schematic representation of an electron "cloud" corresponding to a simple covalent s,s bond; c) schematic representation of an electron "cloud" corresponding to the 2s orbit; d) schematic representation of an electron "cloud" corresponding to the $2p_y$ orbit about the atomic nucleus A.

or of trivalent carbon in carbonium ions, is one electron pair short* of the number required to complete the electron shell of the nearest heavier inert gas

$$\begin{array}{ccc} \overset{\textstyle Br}{\underset{\textstyle Br}{Br:\ddot{B}\check{}}} & \overset{\textstyle Cl}{Cl:\ddot{Al}:Cl} & \underset{\textstyle C_2H_5}{C_2H_5:\overset{+}{C}:CH_3} \end{array}$$

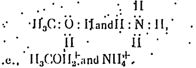
Each hydrogen ion is capable of adding on one electron pair. Quite often metal cations such as Hg^{2+}, Fe^{3+}, Ni^{2+} in solution behave as atoms, capable of participating as acceptors in the formation of several electron pairs. However, in such cases the energy of electrostatic attraction of oppositely charged or easily polarized particles plays an important role, while the acceptor–donor mechanism may be subordinated to it.

Numerous Soviet and foreign investigations have shown that hydrogen linked to oxygen, sulfur, or nitrogen enters isotopic exchange much more easily than hydrogen linked directly to carbon [56-58]. The electron shell

---

*Electron pair deficiency will be denoted by ˇˇ.

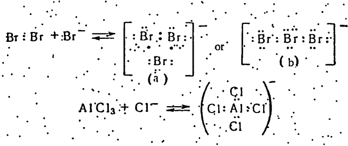
of each quadrivalent carbon atom in organic compounds consists of an octet of four pairs of "occupied" electrons, forming chemical bonds. There are neither free electron pairs nor gaps in the octet. This hinders exchange. Exchange of hydrogen linked with oxygen, sulfur, or nitrogen in organic molecules is easier, because in most cases exchange in solution involves the formation and decomposition of addition complexes with the participation of free electron pairs. For example, in exchange of hydrogen between alcohol and ammonia, the following intermediate groups may be formed



$$H_3C:\ddot{O}:H \text{ and } H:\ddot{N}:H,$$

i.e., $H_3COH_2^+$ and NH_4^+.

In the same way, in rapid isotopic exchange of halide molecules or trivalent metal halides with halide ions, the decisive role is played by reversibly decomposing negatively charged addition complexes



In the gas phase, and in solvents with low dielectric constants these complexes may be neutral, of the form $H^+Br_3^-$. Most acid – base reactions are based on processes of this type. Not only protons and halide ions, but larger groups radicals, ions, and molecules – can pass from molecule to molecule with the participation of free pairs.

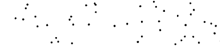
A second feature of electronic structure which facilitates exchange is ease of formation of radicals and biradicals, i.e., particles with one or two unpaired electrons [59]. The third feature is a high degree of electrolytic dissociation with formation of simple ions of the exchanging isotopes, or of polyatomic ions containing them. The emergence of each of these three favorable factors is closely associated with chemical composition and structure, and this relationship is well understood [60]. If the exchanging atoms and groups in one or both of the original compounds are attached to atoms with complete electron octets, then isotopic exchange is generally preceded by transition into one of the active forms discussed above, in which the isotopically exchanging particles are attached to atoms with free electron pairs, or in which unpaired electrons are present, or which are ionized.

1.1 The Role of Tautomeric Regrouping in Isotopic Hydrogen Exchange

Among the preparatory processes for isotopic exchange tautomeric regrouping, reversible ionization, and migration of multiple bonds are very common. As an example, we shall consider the mechanism of the isotopic exchange of hydrogen in acetone. It is found experimentally that the hydrogen of alkyl radicals such as CH_3, C_2H_5, and others in saturated hydrocarbon molecules enters isotopic exchange with water with difficulty. This is also true for many oxygen compounds, such as methyl ether $H_3C:O:CH_3$, in which the carbon of the radical is linked to oxygen. Alkyl radicals adjacent to carbonyl groups of aldehydes and ketones show different behavior. In particular, the rate of exchange of the methyl hydrogen in acetone with water is appreciable even at room temperature, and is sensitive to the pH of the solution. Some authors attribute this to keto – enol tautomerism, the existence of which has been definitely established for acetone and many other saturated compounds containing carbonyl groups

---

*Neither a linear nor a triangular Hal_3^- ion can be designed to conform to the octet rule involving duplet covalent bonds only. The possibility of molecular electrostatic (polarizational) complexes $[Br_2 \cdot Br^-]$ may also be considered. [There is no asterisk corresponding to this footnote in the original – Translator.]



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftarrows CH_2=\overset{\overset{OH}{|}}{C}-CH_3 \qquad (76)$$

The equilibrium concentrations and enol formation rates have been determined for some ketones (see also Chapter IV). Because of this dynamic equilibrium, any of the hydrogens of the methyl group will for some time be present in the hydroxyl and in this position readily enters isotopic exchange with deuterium. As a result, the isotopic hydrogen content in the acetone molecule gradually reaches an equilibrium state corresponding to the molar ratio of acetone and deuterium donor, for a given initial deuterium content in the donor*.

In the limiting case of exchange with a large excess of pure deuterium, the process may be represented as a series of consecutive stages

$$\left.\begin{array}{l}
CH_3-CO-CH_3 \rightarrow CH_3=COH-CH_3 \xrightarrow{DX} \\
\qquad \rightarrow CH_2=COD-CH_3 \rightarrow CH_2D-CO-CH_3, \\
CH_2D-CO-CH_3 \rightarrow CH_2D-COH=CH_2 \xrightarrow{DX} \\
\qquad \rightarrow CH_2D-COD=CH_2 \rightarrow CH_2D-CO-CH_2D, \\
CH_2D-CO-CH_2D \rightarrow CHD=COH-CH_2D \xrightarrow{DX} \\
\qquad \rightarrow CHD=COD-CH_2D \rightarrow CHD_2-CO-CH_2D; \\
CHD_2-CO-CH_2D \rightarrow CD_2=COH-CH_2D \xrightarrow{DX} \\
\qquad \rightarrow CD_2=COD-CH_2D \rightarrow CD_3-CO-CH_2D; \\
CD_3-CO-CH_2D \rightarrow CD_3-COH=CHD \xrightarrow{DX} \\
\qquad \rightarrow CD_3-COD=CHD \rightarrow CD_3-CO-CHD_2; \\
CD_3-CO-CHD_2 \rightarrow CD_3-COH=CD_2 \xrightarrow{DX} \\
\qquad \rightarrow CD_3-COD=CD_2 \rightarrow CD_3-CO-CD_3.
\end{array}\right| \qquad (77)$$

These equations show one of the possible substitution sequences leading to conversion of CH_3COCH_3 into CD_3COCD_3. For simplicity, the following are omitted: 1) reverse processes of exchange with HX, which retard the process; 2) useless transitions of D from the radical into the hydroxyl

$$CH_2D-CO-CH_2D \rightarrow CH_2=COD-CH_2D \rightarrow CH_2D-CO-CH_2D,$$

3) intramolecular redistribution $CH_2D-CO-CH_2D \rightarrow CH_3-CO-CHD_2$, etc. It is important and significant that by this scheme acetone in enol form is capable of exchanging only one hydrogen atom out of the six present in the molecule; therefore in the most favorable case the formation of hexasubstituted acetone requires six-fold repetition of enol formation alternating with its six-fold reconversion into the ketone. In consequence, with normal probability deviations from the mean, consecutive formation of mono-, di-, etc., up to hexadeuteroacetone should occur in the system.

$$C_3H_6O \rightarrow C_3H_5DO \rightarrow C_3H_4D_2O \rightarrow C_3H_3D_3O \rightarrow C_3H_2D_4O \rightarrow C_3HD_5O \rightarrow C_3D_6O. \qquad (78)$$

(This is not essential for exchange involving $CH_3COCH_2^-$ ions.) By interrupting the reaction at a sufficiently early stage, one can obtain a mixture of C_3H_6O and C_3H_5DO without any appreciable traces of fully substituted acetone; at some intermediate duration of the experiment $C_3H_3D_3O$ should predominate, etc. This is a very characteristic distinction from exchange substitution of hydrogen in free radicals, which will be considered later. Mass spectrum investigations of the composition of the exchange products at various stages of the reaction would be very desirable in this connection.

---

*With corrections for the isotopic effects of the equilibrium constant, discussed in Chapter I.

As a second characteristic example of isotopic exchange proceeding by way of reversible isomerization, we may refer to the exchange of hydrocarbon hydrogen, situated far from a double bond in the molecule, with deuteroammonia. This exchange has been systematically studied by Shatenshtein et al. (see §18, Chapter III). To ensure rapid exchange, potassamide, which dissociates reversibly into potassium and amide ions,

$$KND_2 \rightleftarrows K^+ + ND_2^- . \tag{79}$$

was added to the ND_3 which served simultaneously as deuterium donor and solvent. These amide anions exchange hydrogen more easily with most hydrocarbons than do deuteroammonia molecules; and therefore they bring about the reaction directly.

It is probable that ND_2^- acts as a proton acceptor which converts C_nH_{2n} into R^- ions. The latter are converted into RD by the deuterium donor ND_3, regenerating ND_2^- ions:

$$\left.\begin{aligned} C_nH_{2n} + ND_2^- &\rightleftarrows C_nH_{2n-1}^- + ND_2H; \\ ND_3 + C_nH_{2n-1}^- &\rightleftarrows C_nDH_{2n-1} + ND_2^- . \end{aligned}\right\} \tag{80}$$

However, it would be interesting to verify the possibility of direct exchange of ND_2^- with RH without intermediate formation of R^-. The action of catalytic carriers such as KND_3 is typical for isotopic exchange.

Even in presence of potassamide, alkanes practically do not exchange their hydrogen with deuterium of deuteroammonia in conditions in which olefins completely exchange all their hydrogen for deuterium. For example, all 32 hydrogen atoms (!) of cetene, $C_{16}H_{32}$, are exchanged. Therefore, if the double bond is situated at the end of the molecule

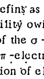
$$\underset{1}{CH_2} = \underset{2-15}{(CH_2)_{14}} - \underset{16}{CH_3}$$

even hydrogen atoms joined to C_{16} separated by 14 single C–C bonds exchange with deuteroammonia. The maximum distance of the methyl group hydrogens is too great for the easy exchange of all the hydrogen of the molecule to be explained by direct or indirect influence of the stationary double bond. The authors were therefore forced to postulate continuous isomerization of the molecule with displacement of the double bond and hydrogen atoms. As a result, cetene-1,2 may pass into cetene-2,3, the latter into cetene-3,4, etc.

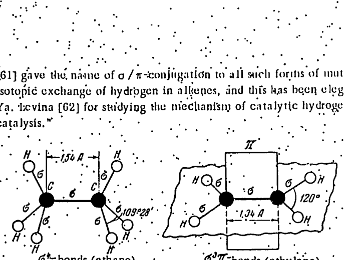
$$\begin{aligned} CH_2 = CH_2 - (CH_2)_{13} - CH_3 \rightleftarrows CH_3 - CH = CH - (CH_2)_{12} - CH_3 \rightleftarrows \\ \rightleftarrows CH_3 - CH_2 - CH = CH - (CH_2)_{11} - CH_3 . \end{aligned} \tag{81}$$

Thus, in addition to the above two reversible reactions (79) and (80), which maintain a mobile chemical and isotopic equilibrium between ammonia, potassamide, and ND_2^- and NHD^- anions in the system, equilibrium between isomeric forms of the olefin of normal structure plays an important part in the exchange. The hydrogen to be actually exchanged is the hydrogen attached to the atom linked by a double bond to its nearest neighbors. It must be emphasized that in the temperature region in which these experiments were performed (20-120°C) individual olefins without catalysts are isomerized too slowly for this mechanism to operate. In ammonia containing KNH_2, the isomerization rate is sufficiently high, and tautomeric forms of the olefins may be assumed to be present.

The cause of the more rapid isotopic exchange in olefins as compared with paraffins is interesting. Carbon atoms directly linked by double bonds have increased mobility owing to the presence of π-electrons, the motion of which within the molecule is quite different from that of the σ-electrons of ordinary electron pair bonds. This is clear from Fig. 48, which shows the positions of σ- and π-electrons in a double bond and σ-electrons of the C–H bond, which to some extent resembles the redistribution of electrons in alternation of single and double bonds in ordinary conjugate bond systems

= — =; 

etc. A.N. Nesmeyanov [61] gave the name of σ/π-conjugation to all such forms of mutual influence. It is a necessary condition for the isotopic exchange of hydrogen in alkenes, and this has been elegantly demonstrated by a method developed by R.Ya. Levina [62] for studying the mechanism of catalytic hydrogen redistribution in N.D. Zelinsky's "irreversible catalysis."



σ⁴-bonds (ethane) σ³π-bonds (ethylene)

Fig. 48. Bond positions in ethane and ethylene, with the special position of the π-electrons of the double bond.

Comparing the numbers of exchanging atoms in unbranched and branched alkanes, the authors showed that the presence in the carbon chain of a quaternary atom, for example, atom 4 in 2,4,4-trimethylpentene-1

$$\underset{1}{CH_2} = \underset{2}{C}(CH_3) - \underset{3}{CH_2} - \underset{4}{C}(CH_3)_2 - \underset{5}{CH_3},$$

practically excludes from the exchange the hydrogen of the three methyl groups at the fourth atom of the chain. In such a molecule formation of a double bond between C_3 and C_4 is impossible, and therefore σ/π conjugation with participation of C–H bonds is excluded for hydrogen of three (of the available four) methyl groups.

As a result, only 7 of the 16 hydrogen atoms are exchanged in practice. Similarly, in the diene $C_{12}H_{22}$ with the structure

$$CH_2 = CH - CH_2 - C(CH_3)_2 - C(CH_3)_2 - CH_2 - CH = CH_2,$$

10 of the 22 hydrogen atoms are exchanged at 100°C in 100 hours. It is natural to expect that H in the part of a molecule blocked on two sides by quaternary atoms will not be exchanged. For example, in the diene $C_{20}H_{38}$ with the structure

$$CH_2 = CH - C(CH_3)_2 - (CH_2)_{10} - C(CH_3)_2 - CH = CH_2$$

not only the 12 atoms of the four methyl groups, but the 20 atoms of the ten middle methylene groups should in practice not participate in exchange facilitated by σ/π-conjugation.

The data presented in this section demonstrate the importance of reversible intramolecular regroupings for isotopic exchange. These regroupings are a special, very common type of formation of intermediate actively exchanging forms, without association or dissociation.

In intramolecular isotopic exchange the whole exchange process can often be reduced to alternate formation and disappearance of such forms. In intermolecular exchange an active isomeric (or tautomeric) form reacts with a deuterium donor by one of the dissociation or association mechanisms described above. Similar situations are found in the isotopic exchange of other elements.

The foregoing examples are instructive in illustrating the very close connection between the ease of isotopic exchange and the electronic structure of molecules. Because of this connection, investigations of isotopic exchange rates have become widely used for studying the structure of organic and inorganic molecules and of their tautomeric transformations. At the same time, the accumulation of experimental data reveals relationships which make it possible to predict the nature and rates of isotopic exchange in new, as yet unstudied systems.

§15. Characteristics of Hydrogen Exchange of Free Radicals and its Role in the Exchange of Saturated Molecules

The development of the chain theory, which attributes to free atoms and radicals a leading role in the kinetics of chemical reactions [63, 64] has shown that a considerable proportion of isotopic exchange reactions probably occurs by an atomic radical mechanism. This has been convincingly proved for homomolecular hydrogen exchange reactions in simple molecules by the early work of the Farkas brothers [35]. Recently the same mechanism was established for the photochemical and electric discharge redistributions of isotopes between homonuclear molecules of oxygen and nitrogen, which are of the chain reaction type. At the pressures and temperatures used in the work, the chain length was considerable (of the order of 10^2).

Elucidation of the role of free atoms and radicals in isotopic exchange of more complex molecules proved to be a much more difficult problem which has been satisfactorily solved, but only in general outline, only very recently. The first experimental data were obtained in the 1930's in connection with the verification of the theory advanced by Rice and others, attributing to aliphatic radicals the leading role in thermal gaseous reactions of hydrocarbons [65]. With the aid of photodissociation sensitized by mercury vapor [66] and electric discharge methods developed by Wood [67] and others [68-70], Boenhoeffer and his school in Germany, Taylor and his associates in the United States, and especially Steacie and his associates in Canada studied, as early as the 1930's, the reactions of deuterium atoms with a number of unsaturated and saturated hydrocarbons [71]. It was found that in absence of ordinary chemical reactions practically no isotopic exchange occurs in the hydrocarbons. In consequence, unsaturated C_2H_4 and C_2H_2 molecules, which can be hydrogenated by molecular hydrogen, exchange in conditions in which ethane and methane are not capable of exchange [72]. With the start of chemical cracking and isomerization isotopic exchange becomes appreciable in saturated hydrocarbons also, but the exchanged deuterium enters almost completely into the chemical reaction products, with unexpectedly high contents of di- and polydeuterated products [73, 74]. For example, when deuterium consisting of a mixture of D atoms and D_2 molecules acts on ethane, the latter contains almost no deuterated molecules on leaving the reaction vessel, while the methane formed by the action of the atoms is very strongly deuterated

$$H_3C-CH_3 + D(+D_2) \begin{cases} \longrightarrow \text{ethane (contains almost no deuterium)} \\ \longrightarrow \text{methane (65-98\% deuterated, with } CD_4 \text{ predominant).} \end{cases}$$

It proved impossible to explain the observed facts in terms of the reactions of saturated molecules. This led to the hypothesis that free aliphatic radicals such as CH_3, C_2H_5 and others, formed by the action of free atoms on saturated molecules, are involved in isotopic exchange. This hypothesis was first developed in detail by Taylor et al. [74], who considered two more special variations. In the first, monoradicals R, which are converted into saturated molecules RH with loss of exchange capacity, are directly exchanged; in the second, mono- and biradicals R and IR participate alternately in the exchange. Equation (82) shows Taylor's mechanism for the formation of deuterated methane.

Primary process of methyl formation

$$\left.\begin{array}{l} 1)\ C_2H_6 \xrightarrow{D} \dot{C}_2H_5 + DH \xrightarrow{D} \dot{C}H_3 + CH_2D + DH, \\ 1a)\ C_2H_6 \xrightarrow{D} CH_3D + \dot{C}H_3 \end{array}\right\} \qquad (82)$$

Monoradical route

$$\left.\begin{array}{l} 2)\ \dot{C}H_3 + \dot{D} \rightarrow CH_3D, \\ 3)\ CH_3D + \dot{D} \rightarrow \dot{C}H_2D + HD, \\ 4)\ \dot{C}H_2D + \dot{D} \rightarrow CH_2D_2, \\ 5)\ CH_2D_2 + \dot{D} \rightarrow \dot{C}HD_2 + HD, \text{ etc,} \end{array}\right\} \qquad (83)$$

Biradical - monoradical route

$$\left.\begin{array}{l} 2)\ \dot{C}H_3 + \dot{D} \rightarrow \dot{C}H_2 + HD, \\ 3)\ \dot{C}H_2 + \dot{D} \rightarrow \dot{C}H_2D, \\ 4)\ \dot{C}H_2D + \dot{D} \rightarrow \dot{C}HD + HD, \\ 5)\ \dot{C}HD + \dot{D} \rightarrow \dot{C}HD_2, \text{ etc.} \end{array}\right\} \qquad (83a)$$

The first variant of this scheme was accepted by most workers who studied radical exchange, up to the end of the 1940's [71, 75].

Serious difficulties arose in attempts to compare quantitatively the observed rates with the rates calculated on the basis of the Taylor–Steacie scheme, which accounted for the main qualitative features of isotopic exchange with the participation of atoms. Reliable quantitative data are now available on the formation kinetics and reactivities of the first members of the homologous series of alkyl radicals (CH_3, C_2H_5, C_3H_7 and iso-C_3H_7, etc.). These data show that reactions proceeding without rupture of the carbon chain, of the type $R + X \rightarrow RH + Y$, and also reactions accompanied by rupture of C–C, C–N, and other bonds, have appreciable activation energies.

Detailed and reliable determinations of the conditions for radical formation were performed by Szwarc [76], who obtained free radicals by pyrolysis of unstable molecules in a stream of an inert gas. Extensive numerical data are contained in Steacie's monograph [71] and his subsequent experimental publications. In his latest monograph, N.N. Semenov [46] gives the values for activation energies and steric factors of the reactions for the simplest aliphatic radicals, given in Table 51.

In this table Q is the heat of reaction ΔH_0, and E is the activation energy. It is seen that the activation energies of the reactions which figure in the first variant of Taylor's scheme are about 12 kcal. According to Majury and Steacie [71], this value for the reaction of CH_3 with D_2 is 11.7 + 0.5 kcal, and for $CH_3D + D$, approximately 11 kcal (see Table 51). However, even with these very low values of E, multiple substitution of three or more H atoms of a radical by D is highly improbable.

TABLE 51

Kinetic Characteristics of Certain Reactions of Free Atoms and Radicals, after N.N. Semenov [46]

Reaction	Q, kcal/mole	E, kcal/mole	Literature
$H + CH_4 \rightarrow H_2 + CH_3$	+2	13	[77,80]
$H + C_2H_6 \rightarrow H_2 + C_2H_5$	+5	9.5	[75]
$D + CH_4 \rightarrow HD + CH_3$	+2	11	[71]
$D + C_2H_6 \rightarrow HD + C_2H_5$	+5	9	[79]
$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	0	11.2	[81]
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	+4	10 4	[81]

Without a detailed analysis of the kinetics of consecutive exchange reactions, which is one of the most difficult problems of the complicated exchange theory (see Chapter V), we shall consider the beginning of the process, when the system is far from isotopic equilibrium and reverse reactions may be neglected. We shall assume for simplicity that the initial mixture consisted of CH_4, D, and D_2. Then the rate of the first stage, analogous to (82, 1)

$$CH_4 + D \xrightarrow{w_1} CH_3 + DH, \qquad (84)$$

may be represented by the equation

$$w_1 = k_1 [CH_4] \cdot [D], \qquad (85)$$

in which the constant

$$k_1 = k_{01}\,\delta \exp[-E/RT], \tag{85a}$$

where k_{01} is the normal preexponential factor; δ is the steric factor; E is the activation energy for reaction (84).

$$\delta \exp[-E/RT] = \gamma \tag{86}$$

is a factor which represents the fraction of the total number of collisions of saturated C_nH_{2n+2} molecules (CH_4 in this instance) with D atoms, leading to formation of C_nH_{2n+1} radicals (CH_3 in this instance) and HD molecules. On our assumptions, the reverse reaction in Taylor's scheme

$$CH_3 + DH \rightarrow CH_4 + D \tag{84a}$$

may be ignored, and all the methyl radicals formed by reaction (84), adding deuterium atoms [see (83, 2)] are converted into deuteromethane CH_3D. The rate of this stage is

$$w_2 = w_1. \tag{87}$$

Stages (3) and (4) of Equation (83) proceed by a similar mechanism, but the rate constant k_3, without allowance for the kinetic isotope effect, should be less by ¼ owing to the decreased number of H atoms in the molecule. Neglecting this, we can write

$$w_4 \doteq w_3 \approx k_1[CH_3D][D]; \tag{87a}$$

or, in view of the practical irreversibility of (84) and (83, 2) (on the assumptions stated),

$$w_4 = w_3 \approx k_1[D]\,w_1 = k_1^2[CH_4][D]^2. \tag{87b}$$

From Equation (86), the square of the factor γ enters Equations (87) and (87a) in implicit form

$$w_4 = w_3 \approx w_{03}\gamma^2.$$

Similarly, the rate equation for stages 5 and 6, leading to formation of trideuteromethane CHD_3, will contain γ^3 and $[D]^3$, etc.

Direct determinations of the activation energy of the isotopic exchange of methane with atomic deuterium, made by a number of authors [71], give values in excess of 11 kcal/mole. The most accurate determinations are probably those of Steacie [77] who found E ≈ 13 kcal/mole for Reaction (84). The steric factor, according to certain authors, is 0.1.* Experimental observations of the exchange kinetics lead to the conclusion that direct exchange by the tetrahedron reversal mechanism

$$CH_4 + D \rightarrow CH_3D + H \tag{88}$$

should be much slower, with an activation energy of not less than 30 kcal. Spectroscopic data lead to the same conclusion [82]. Theoretical calculations based on the intermediate complex theory give a value of 37 kcal/mole [83, 84]. In view of the low accuracy of such calculations, the agreement between theory and experiment must be regarded as good. Steacie assumes a value of 35 kcal/mole for E for this reaction. In the problem under consideration, the fact that the factor

$$\gamma \approx 0.1 \exp[-13\,000/RT].$$

enters the rate constant is important.

---

*In the paper [71] a lower value of E is assumed, of the order of 11 kcal; with $\delta \approx 10^{-3} - 10^{-4}$.

With this value of γ, the formation of disubstituted, and still more so of tri- and quadrisubstituted, deuterated methanes should proceed very slowly even if the deuterium is very largely atomic. In the more usual conditions of thermal exchange the low value of [D] will have an additional effect in lowering the probability and the rate of di- and multisubstitution. This makes exchange according to the Taylor-Steacie scheme improbable. This conclusion was first reached fairly definitely by V.V. Voevodsky in his analysis of the experimental work carried out with G.K. Lavrovskaya, R.F. Mardaleishvili and V.A. Poltorak [84-87] on the isotopic exchange of monoradicals formed by addition of free H atoms to olefins, with molecular deuterium. On the basis of considerations similar to those given above, the authors completely rejected atomic exchange mechanisms, and concluded that an essentially different molecular mechanism predominated in the hydrogen exchange of radicals.

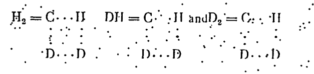
According to V.V. Voevodsky, exchange of hydrogen for deuterium in the methyl radical proceeds according to the scheme

$$\left.\begin{array}{l}\dot{C}H_3 + D_2 \rightarrow \dot{C}H_2D + DH\\ \dot{C}H_2D + D_2 \rightarrow \dot{C}HD_2 + DH\\ \dot{C}HD_2 + D_2 \rightarrow \dot{C}D_3 + DH\end{array}\right\} \tag{89}$$

with ultimate conversion into methane by the reactions

$$\left.\begin{array}{l}\dot{C}H_2D + D_2 \rightarrow CH_2D_2 + D\\ \dot{C}HD_2 + D_2 \rightarrow CHD_3 + D\\ \dot{C}D_3 + D_2 \rightarrow CD_4 + D.\end{array}\right\} \tag{90}$$

The formation of an intermediate complex with internal hydrogen bonds is assumed for the radical reactions



$$\begin{array}{ccc}H_2 = C\cdots H & DH = C\cdots H & \text{and}\ D_2 = C\cdots H\\ \vdots\quad\ \ \vdots & \vdots\quad\ \ \vdots & \vdots\quad\ \ \vdots\\ D\cdots D & D\cdots D & D\cdots D\end{array}$$

In such intermediate molecules there are only five electrons for two bonds between carbon and hydrogen and two inter-hydrogen bonds, and the active part of such a molecule consists of a closed ring of four single electron bonds with the fifth electron oscillating between them. Localization of this fifth electron at the H . . . D bond leads to an exchange reaction, and at the D . . . D bond to decomposition of the complex.

This scheme eliminates one of the difficulties – the repeated participation of D atoms in the exchange – and the observed facts are given a new and interesting explanation [59]. Certain additional relationships were also incidentally established. Thus, it was found that in radicals containing two or more C atoms, H atoms directly linked to the unsaturated carbon are the first to enter into rapid exchange, the H atoms at the β-carbon have considerable capacity for exchange, while the H atoms at the α-carbon exchange only very slightly. Therefore in ethyl $CH_3-\dot{C}H_2$ two hydrogen atoms are exchanged during the reaction, and in isopropyl $CH_3-\dot{C}H-CH_3$ only one. In n-propyl $CH_3-CH_2-\dot{C}H_2$ five atoms are exchanged. According to the mechanism suggested by V.V. Voevodsky, the exchange requires the presence of a free electron at the carbon atom directly linked to the exchanging hydrogen. Therefore it is natural to attribute exchange of hydrogen linked to other atoms to isomerization of the radical, accompanied by proton migration and transfer of an unpaired electron. The exchange of H atoms linked to the β-carbon of the n-propyl radical proceeds by the scheme

$$\begin{array}{ccccccccccc}CH_3 & - & CH_2 & - & \dot{C}H_2 & \rightleftarrows & \dot{C}H_2 & - & CH_2 & - & CH_3\\ 3 & & 2 & & 1 & & 3 & & 2 & & 1\\ \beta & & \alpha & & & & \beta & & \alpha & & \end{array} \tag{91}$$

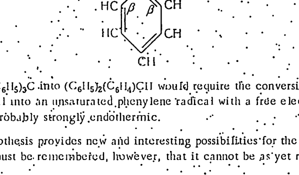
If such mobile equilibrium is established rapidly, the hydrogen of the two end C atoms should exchange almost as rapidly.

From this viewpoint it would be necessary to assume that isomerization with migration of H to adjacent carbon atoms occurs slowly or not at all, i.e., that the following processes are practically absent:

$$\left.\begin{array}{c} \underset{3}{\dot{C}H_3} - \underset{2}{\dot{C}H_2} - \underset{1}{CH_2} \rightleftarrows \underset{3}{CH_3} - \underset{2}{\dot{C}H} - \underset{1}{CH_3} \rightleftarrows \underset{3}{\dot{C}H_2} - \underset{2}{CH_2} - \underset{1}{CH_3} \\ \underset{3}{CH_3} - \underset{2}{\dot{C}H} - \underset{1}{CH_3} \rightleftarrows \underset{3}{\dot{C}H_2} - \underset{2}{CH_2} - \underset{1}{CH_3} \\ \underset{2}{CH_3} - \underset{1}{\dot{C}H} \rightleftarrows \underset{2}{\dot{C}H_2} - \underset{1}{CH_3} \end{array}\right\} \quad (92)$$

With a bent carbon chain the assumption that hydrogen bridges of the type $\begin{array}{l} H_2C - CH_2 \\ \vdots \qquad | \\ H\cdots \dot{C}H_2 \end{array}$ participate in the isomerization makes this picture probable. However, hydrogen in the γ-position and hydrogen at the carbons in positions [illegible] and δ should then exchange still more easily. Further, in radicals with an iso-structure, such as $(CH_3)_3C - \dot{C}H_2$, all the methyl hydrogen, despite the Shatenshtein rule, should exchange easily, etc.

With the aid of a natural additional assumption, Voevodsky's hypothesis can also explain the absence of isotopic exchange of hydrogen in the free radical triphenylmethyl with acetone and water [88]. Triphenylmethyl $(C_6H_5)_3\dot{C}$ has no hydrogen attached to the unsaturated atom. However, each benzene ring contains two hydrogenated carbon atoms in the β-position relative to the $\dot{C}$ atom, and therefore, if hydrogen exchange follows similar laws in alkyl and aryl radicals, rapid exchange of six H atoms and possibly also of the three hydrogens in the para-position relative to the tertiary C atom might be expected in $Ph_3\dot{C}$.



However, isomerization of $(C_6H_5)_3\dot{C}$ into $(C_6H_5)_2(\dot{C}_6H_4)CH$ would require the conversion of a highly symmetrical and very stable phenyl radical into an unsaturated phenylene radical with a free electron at one of the carbons in the ring. This process is probably strongly endothermic.

Thus, Voevodsky's hypothesis provides new and interesting possibilities for the interpretation of old and prediction of new facts; it must be remembered, however, that it cannot be as yet regarded as proved. It is not clear whether the activation energy of the fundamental process $>\dot{C}H + D_2 \rightarrow >\dot{C}D + DH$ would be sufficiently low. For the analogous process $\dot{C}H_3 + C_2H_6 \rightarrow CH_4 + \dot{C}_2H_5$, E is 10 kcal/mole. No direct determinations of E for reactions of this type have yet been made. The rapid exchange of H in the 4,5- and other positions which should follow from this mechanism has not yet been observed or verified. Finally, all the deductions are based on indirect data on the average D contents in the reaction products without direct mass spectrometric investigations of the positions of D in the molecules. These gaps should be filled as soon as possible, with direct verification of the suggested and likely mechanism, which was opposed by Steacie, without adequate grounds, in the second edition of his well known monograph [71].

§16. Ionic Mechanisms of Hydrogen Exchange in Hydrocarbons

Many interesting contributions to an understanding of the mechanism of isotopic exchange have been made by investigations of hydrogen exchange of hydrocarbons with acids. According to the proton transfer theory of acids and bases, proton donors are acids, and proton acceptors are bases. These are not absolute concepts, and the direction of proton transfer depends on the relative strengths of the reacting compounds. The same substance can act as an acid in some conditions and as a base in others. For example, HSO_4^- behaves as an acid toward the acetate ion, the OH^- ion, NH_3, and other substances, converting them into HAc, H_2O, NH_4^+ respectively; but the same HSO_4^- acts as a base with respect to hydrogen chloride, nitric acid, and many other strong acids. The early work of Ingold, Raisin, Wilson [78] and others showed that even at room temperature concentrated sulfuric acid is capable of hydrogen isotope exchange with unsaturated hydrocarbons. With paraffins of normal structure and unsubstituted cycloparaffins the exchange is very slow. The presence of a tertiary carbon atom in the chain [89] or ring greatly facilitates isotopic exchange, and not only the hydrogen at the tertiary atoms is involved. In particular, cyclohexane exchanges very much more slowly than methylcyclohexane with D_2SO_4. According to Burwell and Gordon [90], at 50-60°C both 2-methylheptane (I) and 3-methylheptane (II) exchange hydrogen 100 times as rapidly as normal octane (III):

$$\underset{I}{(CH_3)_2CH - (CH_2)_4 - CH_3}; \quad \underset{II}{CH_3 - CH_2 - CH(CH_3) - (CH_2)_3 - CH_3};$$

$$\underset{III}{CH_3 - (CH_2)_6 - CH_3}$$

In this respect the laws for the exchange of deuterium between hydrocarbons and sulfuric acid greatly resemble the laws for the action of such electrophilic reagents (see below) as nitric acid in nitration, sulfuric acid in sulfonation, or bromine in bromination. There are serious grounds for thinking that this resemblance is based on a similar internal mechanism. Table 52 gives comparative data on the rates of deuterium exchange with D_2SO_4 for a number of hydrocarbons.

TABLE 52

Relative Rates of Isotopic Exchange of Hydrocarbons with 95% D_2SO_4 at 50-60°C, after Gordon and Burwell [90]

Hydrocarbon	Rate in arbitrary units
2-methylpentane, C_6H_{14}	4200
2-methylhexane, C_7H_{16}	2100
2-methylheptane, C_8H_{18}	1200
3-methylheptane	800
n-Octane	7
2,2-dimethylhexane	1
3-methylundecane, $C_{12}H_{26}$	50

The table clearly shows the decisive influence of the presence of a tertiary carbon atom on the exchange rate, and the retardation of exchange with increasing length of the chain. In particular, transition from hexane with one tertiary atom to a similar octane is accompanied by approximately a 4-fold decrease of the rate, while the transition from iso-octane to a hydrocarbon with 12 C atoms of similar structure results in a further 20-fold decrease. The unusual inertness of 2,2-dimethylhexane with a quaternary C atom is striking.

This analogy between deuterium exchange and substitution applies also to aromatic hydrocarbons. The same substituents in the nucleus retard (SO_3H, NO_2, Cl, Br) or accelerate (CH_3, OCH_3, $N(CH_3)_2$) both isotopic exchange with D_2SO_4, and a number of reactions of the electrophilic type. In both cases the substituents influence the rate in the following sequence

$$=O > -NR_2 > -OR > -H > -SO_3H$$

The same rules concerning the predominant direction of the reaction apply in both cases. For example, the presence of halogens, OCH_3 groups and $N(CH_3)_2$ groups attached to carbon atoms of the benzene nucleus directs isotopic exchange and certain substitution reactions predominantly into the ortho- and para-positions with respect to the directing substituent X. On the other hand, in sulfo- and nitrobenzene, hydrogen in the meta-position is more active in deuterium exchange with acids, and halogenation, nitration, and other reactions also occur in this position. In all these cases the strength of the acid is significant, and the sequence of acid donors of deuterium in activity order coincides with their order of strengths [92]

$$D_2SO_4 > D_2SeO_4 > D_3O^+ > CH_3COOD > C_6H_5OD > D_2O$$

Deuterium chloride in presence of aluminum chloride proved to be a very powerful deuterating agent; this mixture acts as the very strong acid $DAlCl_4$ [93]. Addition of water to give a composition corresponding to $[D_3O]^+[HSO_4]^-$ retards exchange both with aliphatic and with aromatic hydrocarbons, therefore the mechanism cannot involve preliminary electrolytic dissociation with exchange between $(D_3O)^+$ or $(DH_2O)^+$ and the hydrocarbon. Substitution of H by D in the ortho- and para-positions has been in some cases precisely demonstrated by displacement of hydrogen by bromination, and spectroscopically [93, 94].

For a fairly long time, exchange between D_2SO_4 molecules and hydrocarbons was believed to proceed by a direct tetramolecular mechanism [58]. This viewpoint is still being upheld by A.I. Brodsky [56]. A special version of this mechanism is the hydrogen bond mechanism postulated by Turkevich and Smith [95, 96]. Gordon and Burwell [97, 98] showed that such schemes are improbable and established the important fact that the reaction is initiated by partial oxidation of hydrocarbons. The unusual stability of 2,2-dimethylhexane and the high mobility of iso-hydrocarbons with one tertiary carbon atom are attributed by these authors to differences in oxidizability. A comparison of the racemization rates of optically active hydrocarbons with rates of isomerization and isotopic exchange led them to the conclusion that the exchange is of a chain character. According to Gordon and Burwell, oxidation creates a small number of initial centers, which result in the exchange of all the hydrocarbon in the system. As a possible common step in the mechanisms of these three reactions, Gordon and Burwell suggest the formation of carbonium ions on oxidation, or oxidative dehydrogenation with formation of unsaturated compounds, the latter mechanism being regarded in the earlier papers as the more probable. In their opinion an argument against the carbonium mechanism is the difficulty of explaining the observed high rates at which adjacent and remote portions of the hydrocarbon chain are drawn into hydrogen exchange, and the absence of a parallelism between the intensity of color formed in mixtures of H_2SO_4 with iso-C_nH_{2n+2} [97], which has long been attributed to the carbonium ion, and the isotopic exchange rates as shown in Table 52. The doubts expressed in these papers concerning the validity of the carbonium mechanism are not of a categorical nature and are based on indirect data. At the same time the juxtaposition of the olefin and carbonium mechanisms can hardly be justified, as one of the main features of the carbonium theory is the ease of formation of carbonium ions by proton (or deuteron) addition at the double bond [98, 99]. Therefore, if formation of $R_1CH = CHR_2$,* is assumed, it is difficult to explain the absence of the reaction

$$R_1CH = CH - R_2 + D_2SO_4 \rightarrow (R_1CHD - \overset{+}{C}H - R_2)^{\oplus}(OSO_3D)^{\ominus}. \qquad (93)$$

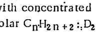
The mechanism of isotopic exchange between deutero acids and hydrocarbons has been studied further in extensive work carried out in D.N. Kursanov's and A.I. Shatenshtein's laboratories, recently published in the USSR, and in the work of American investigators studying the mechanism of acid catalysis.

The catalysts of the acid-base type used in hydrocarbon reactions are mainly strong liquid protonic acids such as H_2SO_4, H_3PO_4, HF, solid compounds with an acidic function, such as aluminosilicates and aluminotitanates, and halides of tri- and quadrivalent metals. The first studies of isotopic exchange of hydrocarbon hydrogen with the use of liquid and solid acid catalysts showed that with a given catalyst exchange usually begins at a temperature considerably below the temperature at which appreciable catalytic cracking commences, and near the temperatures of certain catalytic isomerization reactions. In general unsaturated compounds enter more readily than saturated into isotopic exchange. The ease of exchange greatly depends on the structure of the carbon chain.

Considerable interest attaches, in this connection, to the studies of hydrogen exchange in a large number of hydrocarbons, published in recent years by D.N. Kursanov jointly with V.N. Setkina, O.D. Sterligov and A.L. Liberman [102, 103]. The exchange of saturated hydrocarbons with concentrated deuterosulfuric acid was studied. The experiments were performed at room temperature with molar $C_nH_{2n+2} : D_2SO_4$ ratios from 1 : 1 to 1 : 3. It was found that in these conditions hydrocarbons without tertiary carbon atoms were completely incapable of isotopic exchange. Thus, no exchange was found in n-hexane, n-dodecane, 2,2-dimethylhexane, cyclohexane, 1,1-dimethylcyclohexane, and others. None of the molecules of these hydrocarbons contain methine groups, CH

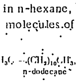
$H_3C-(CH_2)_4-CH_3$
n-hexane

$H_3C-(CH_2)_{10}-CH_3$
n-dodecane



$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-(CH_2)_3-CH_3$

2,2-dimethylhexane

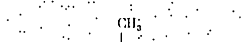


cyclohexane

---

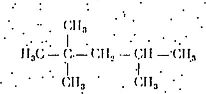
*Recently Burwell has joined the supporters of the carbonium exchange mechanism [100, 101].

On the other hand, hydrocarbons containing tertiary methine carbon atoms, such as



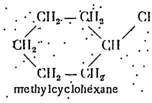
$H_3C-CH_2-\overset{CH_3}{CH}-(CH_2)_2-CH_3$,

3-methylhexane



$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{CH}-CH_3$

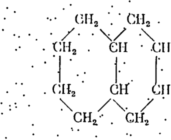
2,2,4-trimethylpentane



methylcyclohexane

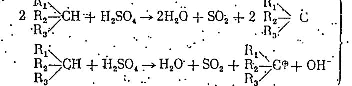
readily participate in exchange.

In the conditions used in these investigations, all the hydrogen in the molecule and not only the methine hydrogen takes part in the exchange. An exception to this rule is decalin,



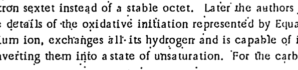
the hydrogen of which is not exchanged despite the presence of two methine groups. The authors attribute the anomalous behavior of hydrogen in this compound to "shielding" of the methine groups by the rings situated on both sides, which is not very likely.

The formation, in isotopic exchange, of small amounts of SO_2 and of intermediate colored compounds, and also the fact that no exchange occurs with acids without oxidizing properties, makes the authors assume that oxidation of methine hydrogen is the initiation stage of the process. This agrees with Gordon and Burwell's early conclusions. In Kursanov's first papers two variants of such initiation are examined



$$\left.\begin{array}{l} 2\begin{matrix}R_1\\R_2\\R_3\end{matrix}\!>\!CH + H_2SO_4 \rightarrow 2H_2O + SO_2 + 2\begin{matrix}R_1\\R_2\\R_3\end{matrix}\!>\!\dot{C} \\ \begin{matrix}R_1\\R_2\\R_3\end{matrix}\!>\!CH + H_2SO_4 \rightarrow H_2O + SO_2 + \begin{matrix}R_1\\R_2\\R_3\end{matrix}\!>\!C^{\oplus} + OH^{-} \end{array}\right\} \qquad (94)$$

In the first case an uncharged monoradical is formed; in the second, a carbonium ion with a trivalent carbon atom surrounded by an electron sextet instead of a stable octet. Later the authors gave final preference to the carbonium mechanism [59]. The details of the oxidative initiation represented by Equation (94) are not clear. The monoradical, or the carbonium ion, exchanges all its hydrogen and is capable of introducing new saturated molecules into the reaction, converting them into a state of unsaturation. For the carbonium variant this may be written as



$$\begin{matrix}R_1\\R_2\\R_3\end{matrix}\!>\!C^{\oplus} + H-\underset{R_2}{\overset{R_1}{C}}-R_3 \rightarrow \begin{matrix}R_1\\R_2\\R_3\end{matrix}\!>\!CH + \underset{R_2}{\overset{R_1}{\overset{\oplus}{C}}}-R_3 \qquad (95)$$

We must point out that in the experimental conditions used by D.N. Kursanov and his associates only extremely ent hydrogen atoms could escape exchange, and finer distinctions of reactivity, associated with relative proximity to the ionized C atom, could not be detected.

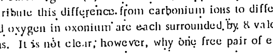
The sensitivity of the isotopic exchange rate to molecular structure, and the unexpected effects which may occur are demonstrated by the work of D.N. Kursanov and Z.N. Parnes on the exchange of hydrogen in α- and β-unsaturated ketones in dioxane solutions [105]. Earlier work had shown that the presence of multiple bonds greatly assists isotopic exchange. Olefins exchange more easily than paraffins, and acetylenic derivatives more easily than olefins. Saturated ketones exchange rapidly and completely all the hydrogen linked to the carbon adjacent to the carbonyl group. This led the authors to the hypothesis that unsaturated ketones containing a methine group at the double bond, simultaneously linked to the carbonyl, such as dibenzylacetone $C_6H_5CH = CH - CO - CH = CHC_6H_5$, should exchange especially easily. In reality, isotopic exchange could not be detected in compounds of this type.

The same group of scientists performed additional investigations to verify the hypothesis of carbonium ion formation in exchange, and of the decisive role of carbonium ions.

Deuterium exchange was studied in organic compounds known to give saltlike products with mineral acids. The carbonyl compounds studied were ketones and carboxylic acids [106]. In the latter, only the hydrogen linked to the carbon adjacent to the carbonyl group is exchanged with deuterium of concentrated sulfuric acid. In acetic (I), propionic (II), and isomeric butyric acids (III) and (IV)

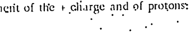
$$\underset{I}{CH_3COOH};\quad \underset{II}{CH_3 - CH_2 - COOH};\quad \underset{III}{(CH_3)_2 - CH - COOH};\quad \underset{IV}{(CH_3)_3C - COOH}$$

3, 2, 1, and 0 H atoms respectively were exchanged. For the exchange of ketones and carboxylic acids with D_2SO_4, the authors postulate the formation of an ionic compound



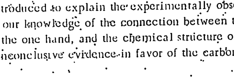
$$\begin{matrix}R_1\\ \\R_2\end{matrix}\!\!>C = O + D_2SO_4 \to \left[\begin{matrix}R_1\\ \\R_2\end{matrix}\!\!>\overset{\oplus}{C} - OD\right]^+ \cdot DSO_4^- \qquad (96)$$

in the first stage, with subsequent exchange of H contained in R_1 and R_2. The selectivity of the exchange indicates that isomerization and displacement of positive charge and unsaturation do not occur in such ionic radicals. Isotopic hydrogen exchange within other organic (+) ions either of the ammonium or of the oxonium type is completely absent. The authors attribute this difference from carbonium ions to differences in the electron shells. The nitrogen in ammonium and oxygen in oxonium are each surrounded by 8 valence electrons, while carbonium carbon has only 6 such electrons. It is not clear, however, why one free pair of electrons of the oxygen atom in the oxonium ion is not used for exchange



carbonium ammonium oxonium

To explain the complete exchange of all the hydrogen atoms in hydrocarbons, D.N. Kursanov postulates isomerization of the radical with displacement of the + charge and of protons:



(97)

In his view, the presence of the carbonyl group renders the (+) charge immobile. All these more or less convincing hypotheses must be introduced to explain the experimentally observed relationships. Therefore these investigations, while they extend our knowledge of the connection between the ease of isotopic exchange and the number of exchanging atoms, on the one hand, and the chemical structure of the exchanging compound on the other, provide only indirect and inconclusive evidence in favor of the carbonium mechanism of deuterium exchange.

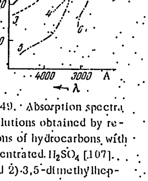
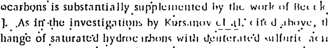


Fig. 49. Absorption spectra of solutions obtained by reactions of hydrocarbons with concentrated H_2SO_4 [107]. 1 and 2) 3,5-dimethylheptane; 3 and 4) methylcyclohexane; 5 and 6) trimethyl carbinol; 1, 3, 5) in concentrated H_2SO_4; 2, 4, 6) after dilution with ethanol.

More promising in this respect was the work of the same group on the absorption spectra, in the visible and ultraviolet regions, of hydrocarbon solutions in mineral acids. As has already been noted, when hydrocarbons capable of deuterium exchange react with concentrated sulfuric acid, the sulfuric acid layer, and the whole solution if the hydrocarbon is sufficiently soluble, acquires a characteristic pink color. I.I. Lavrushin, D.N. Kursanov, and V.N. Setkina [107] showed that the spectra of such colored solutions had characteristic absorption bands in the 2930-2950 A and 2270-2300 A regions, shown in Fig. 49, for all the hydrocarbons studied by them. The figure shows that similar bands, with absorption maxima at almost exactly the same wave lengths, are given by solutions of tertiary alcohols in sulfuric acid, in which formation of carbonium ions is highly probable:



$$R_1 - \overset{\overset{R_3}{|}}{C}OH - R_2 + H_2SO_4 \to R_1\overset{\overset{R_3}{|}}{C}{}^{\oplus} - R_2 \cdot HSO_4^- + H_2O \qquad (98)$$

Our knowledge of the nature of the interaction of strong mineral acids with hydrocarbons is substantially supplemented by the work of Beeck et al [108, 109]. As in the investigations by Kursanov et al. cited above, the isotopic exchange of saturated hydrocarbons with deuterated sulfuric acid was studied. After sufficiently prolonged contact all the deuterium introduced into the system in the form of D_2SO_4 should become distributed between the hydrocarbon and the acid in accordance with the values of the equilibrium constants which, both for the exchange of the first hydrogen atom

$$\left.\begin{aligned}C_nH_{2n+2} + D_2SO_4 &\to C_nH_{2n+1}D + DHSO_4,\\ C_nH_{2n+2} + DHSO_4 &\to C_nH_{2n+1}D + H_2SO_4,\end{aligned}\right\} \qquad (99)$$

and for the exchange of the subsequent atoms (with formation of $C_nH_{2n}D_2$, $C_nH_{2n-1}D_3$, etc.) do not greatly differ from unity.* The relative numbers of hydrocarbon molecules containing different numbers of deuterium atoms in their molecules:

$$C_nH_{2n+2},\ C_nH_{2n+1}D,\ C_nH_{2n}D_2 \text{ and up to } C_nD_{2n+2}$$

inclusive are largely determined by the ratio of the total number of deuterium atoms ΣD to the total number of protium atoms ΣH in the system as a whole. At a low value of the $\Sigma D/\Sigma H$ ratio and when equilibrium has been established, $C_nH_{2n+1}D$ molecules should predominate among the deuterated hydrocarbon molecules, while the number of molecules with a higher D content should decrease rapidly with increasing numbers of D atoms in these molecules.

With a low content of H in the system, on the contrary, molecules containing one atom of hydrogen each should decisively predominate among the molecules of mixed isotopic composition. With similar contents of protium and deuterium, the equilibrium curves showing the relative contents of molecules of different isotopic compositions show maxima, the heights and positions of which depend on the value of the $\Sigma H/\Sigma D$ ratio. The molecular composition of the system at ideal isotopic equilibrium can be easily calculated by the theory of probability. The calculation of the equilibrium fraction ρ of molecules which contain some number x atoms of a given isotope, for a total constant number k of atoms of the given element in the molecule, is analogous to the problem, solved long ago, of the probability of obtaining x white and $k-x$ black balls in removing consecutively k balls from a box containing a very large number of black and white balls. The same probability methods are

---

*Direct determinations of these values for certain hydrocarbons and various strong deutero acids and also for deuteroammonia are reported in papers by A.I. Shatenshtein, E.A. Izrailevich, et al. [110] They give α 0.9 (see Chapter I, §19, c).

used for solving more complex problems on the equilibrium contents of molecules with different arrangements of deuterium and protium, and on ρ for systems containing three or more isotopes. Corrections for nonideality of all isotopic equilibria can be easily introduced into the corresponding formulas.

For our particular case of the isotopic composition of hydrocarbons with protium and deuterium present in the system, mathematical analysis based on the probability theory leads to a formula which gives the relative content at equilibrium, of molecules containing x deuterium atoms with a total of k hydrogen atoms in the molecule

$$\rho_x^k = \frac{k!}{x!(k-x)!}\left(\frac{\Sigma H}{\Sigma H + \Sigma D}\right)^{k-x}\left(\frac{\Sigma D}{\Sigma H + \Sigma D}\right)^x \quad (100)$$

and

$$\frac{\Sigma H}{\Sigma D} = \frac{kN_{hyd.}}{2N_{D_2SO_4}}, \quad (100a)$$

where $N_{hyd.}$ is the number of moles of hydrocarbon; $N_{D_2SO_4}$ is the number of moles of deuterosulfuric acid in the system. For isobutane k = 10, and Equation (100) may be written as

$$\rho_x^{10} = \frac{10!}{x!(10-x)!}\left(\frac{\Sigma H}{\Sigma H + \Sigma D}\right)^{10-x}\left(\frac{\Sigma D}{\Sigma H + \Sigma D}\right)^x \quad (100b)$$

or

$$\rho_x^{10} = \frac{10!}{x!(10-x)!}(\gamma_H)^{10-x}(\gamma_D)^x. \quad (100c)$$

The situation is different with contact times insufficient for an approach to isotopic equilibrium. In such cases, under favorable conditions, it may prove possible to detect deviations in the isotopic compositions of the hydrocarbons which depend on the kinetics of the process and reflect its deep mechanism. On these considerations, Otvos, Stevenson, Wagner and Beeck [108, 109] studied the isotopic composition of hydrocarbons obtained at early stages of isotopic exchange of alkanes, alkenes, and cycloalkanes containing from four to seven carbon atoms in the molecule. In most of the experiments 2 ml (i.e., about 40 millimoles) of 95% D_2SO_4, obtained by the action of SO_3 on D_2O, and 0.6 millimole of the hydrocarbon were introduced into a glass bulb, this was sealed and shaken for a definite time at 25° or 0°C; the hydrocarbons were then distilled off and their chemical and isotopic composition determined. These experiments, in complete agreement with the results of Ingold et al. [78, 92], Gordon and Burwell [90, 91], and V.N. Setkina, D.N. Kursanov, O.D. Sterligov and A.L. Liberman [102], showed sharp differences between paraffins of normal and iso structure in the isotopic exchange rates. The former did not enter into isotopic exchange at all in the conditions used. Only alkanes and cycloalkanes containing at least one tertiary carbon atom were capable of exchange. At the same time, only these hydrocarbons undergo isomerization under the action of sulfuric acid at 25°C. This indicates a close relationship between isotopic exchange and isomerization. For the molar proportions used, ΣD : ΣH for butane is approximately 13. For heptane this ratio is a little below 8. If the exchange has a simple bimolecular mechanism, in its initial stage the appearance of $C_nH_{2n+1}D$ molecules should be expected in alkanes and of $C_nH_{2n-1}D$ molecules in cycloalkanes, with formation of small concentrations of deuterated molecules with high D contents, such as C_nD_{2n+2} or $C_nD_{2n+1}H$ for alkanes and C_nD_{2n} and C_nD_{2n-1} for cycloalkanes only at the end of the exchange. In reality, even at the very beginning of the exchange, when 95% and over of the hydrocarbon molecules do not contain deuterium, highly deuterated molecules definitely predominate in the exchange products. In particular, in the case of iso-butane, in which three methyl groups are attached to a tertiary carbon atom, iso-C_4D_9H and iso-$C_4D_8H_2$ predominate in the products, and iso-C_4H_9D and iso-$C_4H_8D_2$ are practically absent.

Super-equilibrium contents of polysubstituted molecules have often been observed in recent years by mass spectroscopy in ordinary and catalytic deuterium exchange of hydrocarbons. It is proved in the theory of complicated isotopic exchange (see Chapter V) that the presence of molecules with sharply different exchange capacities is at the root of this effect. Under suitable conditions, molecules of one type, active with respect to exchange, are able to exchange their hydrogen completely before the isotopic composition of the hydrogen in slowly exchanging molecules has changed appreciably. While this condition is satisfied, the contents of forms of different deutero-substitution are determined by the ratio of ΣD to the total content of ordinary hydrogen Σ^*H in active molecules, $\frac{\Sigma D}{\Sigma^* H}$, which is greater than $\frac{\Sigma D}{\Sigma H}$ in consequence of the inequality $\Sigma H \gg \Sigma^* H$. The ratio $\frac{\Sigma D}{\Sigma^* H} / \frac{\Sigma D}{\Sigma H}$ is greater with smaller contents of rapidly exchanging molecules in the system. Of course, there should not be any considerable exchange between deuterated and undeuterated acceptor molecules with omission of the donor. Since in the American work the exchange took place in simple binary systems, each consisting of one pure individual hydrocarbon and one donor (D_2SO_4), mixtures containing two or several deuterium acceptors could be formed only as the result of additional chemical action between the hydrocarbon and the acid. This led the authors to postulate the scheme shown below. The great prevalence of highly substituted products at the start of the reaction was interpreted as an indication of a low content of active molecules. The hydrocarbon, by a little understood chemical reaction with sulfuric acid, loses its tertiary carbon and is converted into a radical which exchanges its hydrogen for deuterium of much less saturated molecules. In the case of isobutane the labile radical is apparently iso-C_4H_9, solvated by sulfuric acid molecules, iso-$C_4H_9 \cdot nD_2SO_4$. On the basis of certain indirect data these authors, like Kursanov and his associates, identify this radical with carbonium, i.e., attributing a (+) charge at the tertiary carbon atom to the iso-C_4H_9 radical. For formation of such a radical, a molecule must lose a proton and two electrons, i.e., a hydride ion (:H). This occurs mainly with the hydrogen of the tertiary C atom, which is more electropositive than primary or secondary carbon atoms, and the hydrogen of which is therefore more electronegative. The same carbonium radical would be obtained by addition of a proton to the corresponding olefin in exchange of the latter with D_2SO_4

$$\left.\begin{aligned} &\text{iso-}C_4H_{10} \rightarrow C_4H_9^{\oplus} + H^{\ominus}, \\ &\text{iso-}C_4H_8 + H^{\oplus} \rightarrow \text{iso-}C_4H_9^{\oplus}. \end{aligned}\right\} \quad (101)$$

If this radical readily enters isotopic exchange with deuterium and has a sufficiently long life, it is able to exchange all its hydrogen before again becoming an ordinary saturated hydrocarbon molecule. In these conditions the series of consecutive substitution reactions may be completed before the formation of an appreciable number of new primary $C_4H_9^{\oplus}$ carbonium ions. At a high D_2SO_4 content the conversion of a considerable proportion of $C_4D_9^{\oplus}$ radicals into stable C_4D_{10} molecules might be expected. In reality, fully deuterated hydrocarbons are practically absent even at very high contents of molecules in which 2n + 1 H atoms have been replaced by deuterium. The authors explain this by the ingenious suggestion that $C_4H_9^+$ and all its deuterated analogs up to $C_4D_9^+$ inclusive disappear practically only by removal of hydride hydrogen from the tertiary atom of a new hydrocarbon molecule

$$\text{iso-}C_4^{\oplus}D_9 + \text{iso-}C_4H_{10} \rightarrow \text{iso-}C_4HD_9 + \text{iso-}C_4^{\oplus}H_9 \quad (102)$$

Since at the beginning of the exchange the latter contain no deuterium, a stable C_4HD_9 molecule and a new $C_4H_9^+$ radical are formed, and the latter begins a new series of exchange reactions. Thus, a peculiar chain mechanism is postulated as the result of a study of the exchange products. One H atom after another within each active molecule is replaced by deuterium by a chain mechanism, and a slower chain transfer between molecules is superposed on this. The carbonium radical serves as an active particle in both types of chain. The initial iso-$C_4H_9^+$ centers are formed as the result of some side process of oxidation, not well understood (this is doubtful in the light of the work of Shatenshtein et al. [104]). Their accumulation is prevented by side processes of polymerization, and the principal chain has the form.

$$\left.\begin{aligned} &1)\ \text{iso-}C_4^{\oplus}H_9 + D_2SO_4 \rightarrow \text{iso-}C_4^{\oplus}H_8D + DHSO_4, \\ &2)\ \text{iso-}C_4^{\oplus}H_8D + D_2SO_4 \rightarrow \text{iso-}C_4^{\oplus}H_7D_2 + DHSO_4, \\ &3\text{—}8)\ \ldots \\ &9)\ \text{iso-}C_4^{\oplus}HD_8 + D_2SO_4 \rightarrow \text{iso-}C_4^{\oplus}D_9 + DHSO_4, \\ &10)\ \text{iso-}C_4^{\oplus}D_9 + \text{iso-}C_4H_{10} \rightarrow \text{iso-}C_4D_9H + \text{iso-}C_4^{\oplus}H_9, \\ &1')\ \text{iso-}C_4^{\oplus}H_9 + D_2SO_4 \rightarrow \text{iso-}C_4^{\oplus}H_8D + DHSO_4, \\ &2')\ \text{iso-}C_4^{\oplus}H_8D + D_2SO_4 \rightarrow \text{iso-}C_4^{\oplus}H_7D_2 + DHSO_4 \end{aligned}\right\} \quad (103)$$

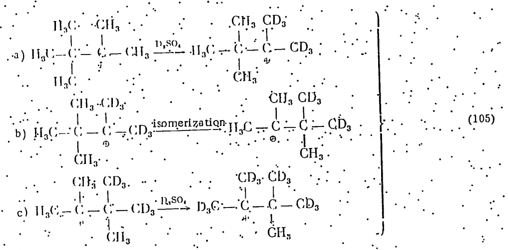
etc.

If this mechanism is to lead to the experimentally observed results, the probability of the process (10) in [illegible] (103) should be much lower than the probability of the rapid processes (1-9) in the same equation. The probability of new chain initiation must be lower still. Many results are in good agreement with this interesting [illegible], the authors consider that it is confirmed by: 1) acceleration of the exchange and disappearance of the induction period on addition of butylene, in the presence of which a new source of carbonium ions appears:*

$$\text{iso-}C_4H_8 + H^{\oplus} \rightarrow C_4H_9^+ \text{ or } \text{iso-}C_4H_8 + D^{\oplus} \rightarrow \text{iso-}C_4H_8D^+; \quad (104)$$

[illegible] increase of the relative content of the $C_nD_{2n+1}H$ product when the concentration of deuterated sulfuric acid is lowered, 3) conversion of artificially introduced monodeuterated molecules into polydeuterated, with simultaneous formation of 20-30% of the same isomer not containing deuterium;** 4) Burwell and Gordon's data [90, [illegible]] on the racemization of optically active 3-methylpentane, which occurs in parallel with isotopic exchange.

According to the American authors, deuterium exchange is always accompanied by isomerization in hydrocarbons with more than 4 carbon atoms, and in some instances the rates of these processes calculated on the number of carbonium ions formed coincide, while in others isomerization is considerably slower than isotopic exchange; [illegible] with D_2SO_4, every isomerization is accompanied by isotopic exchange, but not every isotopic exchange is accompanied by isomerization. The behavior of solid catalysts is different – in their presence isomerization may occur under certain conditions without appreciable isotopic exchange. According to Beeck et al. [108, 109], the hydrogen atoms linked to different carbon atoms in substituted butanes participate unequally in exchange. The hydrogen atoms linked to the carbons adjacent to the tertiary atom are easily exchanged completely, and this determines the minimum number of exchanging atoms. In this respect charged radicals in solutions are apparently unlike the neutral gaseous radicals in Voevodsky's experiments. On isomerization of the carbon chain, more distant carbon atoms may also become adjacent, and therefore, in the case of pentanes to heptanes, all the hydrogen atoms can be replaced with the exception of the single atom linked to the tertiary carbon at the instant when the carbonium [illegible] is converted into ordinary carbon. Thus, for example, in trimethylbutane the minimum number of hydrogen atoms initially exchanged according to Equation (105a) is six. These six atoms are in methyl groups occupying α-positions with respect to $C^{\oplus}$. By isomerization of the carbonium ion according to Equation (105, b) [illegible] more atoms become capable of exchange, and the total number of exchanging atoms becomes 12



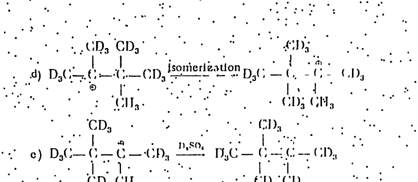
$$\left.\begin{array}{l}
a)\ H_3C-\underset{H_3C}{\overset{H_3C}{C}}-\underset{\oplus}{\overset{CH_3}{C}}-CH_3 \xrightarrow{D_2SO_4} H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\oplus}{\overset{CD_3}{C}}-CD_3\\
b)\ H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\oplus}{\overset{CD_3}{C}}-CD_3 \xrightarrow{\text{isomerization}} H_3C-\underset{\oplus}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CD_3}{C}}-CD_3\\
c)\ H_3C-\underset{\oplus}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CD_3}{C}}-CD_3 \xrightarrow{D_2SO_4} D_3C-\underset{\oplus}{\overset{CD_3}{C}}-\underset{CH_3}{\overset{CD_3}{C}}-CD_3
\end{array}\right\} \quad (105)$$

---

*In concentrated solutions the process (104) occurs with participation of acid molecules and not dissociated protons

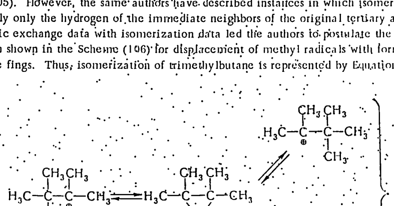
$$C_4H_8 + D_2SO_4 \rightarrow C_4H_8D^+ + DSO_4^{\ominus}.$$

**Details of this peculiar process are not given, and its actual mechanism is not clear.



$$\begin{array}{l}
d)\ D_3C-\underset{\oplus}{\overset{CD_3}{C}}-\underset{CH_3}{\overset{CD_3}{C}}-CD_3 \xrightarrow{\text{isomerization}} D_3C-\underset{CD_3}{\overset{CD_3}{C}}-\underset{CH_3}{\overset{\oplus}{C}}-CD_3\\
e)\ D_3C-\underset{CD_3}{\overset{CD_3}{C}}-\underset{CH_3}{\overset{\oplus}{C}}-CD_3 \xrightarrow{D_2SO_4} D_3C-\underset{CD_3}{\overset{CD_3}{C}}-\underset{CD_3}{\overset{\oplus}{C}}-CD_3
\end{array} \quad (105)$$

Finally, after new isomerization according to Equation (105,d), the last three H atoms react according to Equation (105,e), and the exchange includes all 15 hydrogen atoms of the iso-$C_7^{\oplus}H_{15}$ carbonium ion. Experiments show that at 25°C molecules with fifteen deuterium atoms predominate in the products. According to the suggested explanation this composition means that the average life of the trimethylbutane carbonium ion in the experimental conditions used is considerably longer than the average time required for the isomerization processes shown in Equation (105). However, the same authors have described instances in which isomerization proceeds slowly, and practically only the hydrogen of the immediate neighbors of the original tertiary atom is replaced. Comparison of isotopic exchange data with isomerization data led the authors to postulate the peculiar and highly debatable mechanism shown in the Scheme (106) for displacement of methyl radicals with formation of intermediate trimethylene rings. Thus, isomerization of trimethylbutane is represented by Equation (106):



(106)

Very recently Burwell et al. [100, 101] have published new interesting data on the ratios between the racemization and isomerization rates of hydrocarbons under the action of deuterosulfuric and chloro- and fluorosulfonic acids. The basic concept of a chain process involving carbonium ions received further confirmation by this, but at the same time facts were found indicating the existence of complications not accounted for by the scheme.

The findings of the Soviet and the American workers differ with regard to the participation in isotopic exchange of the hydrogen at the tertiary C atom and of hydrogen linked to the β-, γ-, and other atoms still further removed from the tertiary carbon. According to Beeck, the hydrogen at the tertiary atom is not exchanged at all, and according to Kursanov it is exchanged completely. According to Beeck, the hydrogen of the remote carbon atoms exchanges more slowly than the hydrogen linked to α-carbon atoms, and this exchange can be avoided, according to Kursanov, the remote atoms exchange completely. The first discrepancy is only apparent. Beeck chose conditions in which only part of the H entered the exchange, and therefore he was able to detect differences in exchange capacity which escaped in Kursanov's exchange, which was nearly 100%. It seems likely that in the latter's experiments also C_4D_9H molecules were first formed and these, despite the slow conversion, had time to pass into C_4D_{10}. It is equally possible that in Kursanov's experiments the heavier hydrocarbons first yielded molecules with deuterium only at the α-carbon, and the remaining hydrogen entered the exchange as the result of isomerization. It is more difficult to explain the discrepancy in the data on the relative ease of exchange of hydrogen at the α- and β-carbon (relative to C$^{\oplus}$) found by the American workers and by Voevodsky, who made direct studies of isotopic exchange of hydrogen in free radicals. It is unlikely that the mere presence of a positive charge can cause such differences. We must also emphasize the sharp difference between the views of the Soviet and American scientists on the actual isomerization mechanism which draws remote hydrogen into the exchange. According to Kursanov and Voevodsky this is simple migration of the hydride ion, causing displacement of the (+) charge, the intramolecular analog of the mechanism, accepted by both groups of workers, by which active molecules (carbonium ions) draw inactive molecules into the exchange [see Equation (102)], while according to Beeck, Otvos, and Stevenson it is isomerization of the carbon chain of the molecule, proceeding through closing and opening of three-membered rings. Although this last isomerization mechanism in itself arouses doubt, as the first stage of trimethylene ring closing is highly endothermic, the paper as a whole is a good illustration of the useful results gained by studies of the distribution of molecules with different degrees of deuterium substitution among the reaction products in order to determine the true exchange mechanism. Termination of the exchange at low degrees of conversion, whereby it is possible to detect important features of the process which are not revealed when the process is far advanced, is also a progressive research method.

The different researches on the isotopic exchange of hydrocarbons containing tertiary carbon atoms in their molecules jointly confirm to some extent the highly popular but until recently speculative carbonium hypothesis. This is important for understanding the mechanisms of a large group of chemical reactions of hydrocarbons, including cracking, alkylation, isomerization, and some instances of polymerization. In some recent publications the reality of the carbonium radical has been confirmed by cryoscopic and spectroscopic determination. Cryoscopic determinations were carried out by Gold, Hawes and Tye [111] on solutions of a number of hydrocarbons and alcohols in concentrated sulfuric acid. 1,1-diphenylethylene $(C_6H_5)_2C = CH_2$ and 1-naphthyl-1-phenylethylene $(C_{10}H_7)(C_6H_5)C = CH_2$ gave double the theoretical values of the molecular freezing point depression [111, 112]. In the case of alcohols, in particular of diphenyl carbinol, the molecular depression was four times the normal value. To explain these results, the authors postulate electrolytic dissociation processes involving sulfuric acid molecules, represented by the Equations (107).

$$\left.\begin{array}{l} Ph_2C = CH_2 + H_2SO_4 \rightarrow Ph_2C^{+} - CH_3 + HSO_4^{-}, \\ Ph_2MeCOH + 2H_2SO_4 \rightarrow Ph_2MeC^{+} + H_3O^{+} + 2HSO_4^{-} \end{array}\right\} \qquad (107)$$

The absorption spectra of these solutions in the ultraviolet region were sharply different from the spectra of the corresponding individual hydrocarbons, the differences exceeding the usual effects of the solvents. The spectra of diphenylethylene, triphenylethylene, anthracene, and 1-naphthyl-1-phenylethylene dissolved in sulfuric acid show similar absorption bands, which are interpreted as spectra of carbonium ions of an analogous electronic structure (Fig. 50).

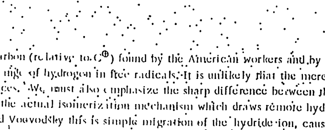


Fig. 50. Carbonium ion scheme, after Gold.

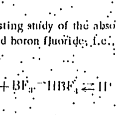
We note in this connection that all the hydrocarbons studied are conjugated multiple bond systems and that their absorption spectra are associated with π-electrons.

It is clear that there is a great deal of similarity between Gold and Tye's findings and the results of the work of I.I. Lavrushin, D.N. Kursanov and V.N. Setkina [107] discussed on page 171. However, the English workers used aromatic hydrocarbons while the Soviet workers used aliphatics. Gold augmented the optical data cryoscopically, and Lavrushin and his associates by comparison with absorption spectra of sulfuric acid solutions of carbinols. This shows that the results obtained are general and representative. However, there are some debatable points in the authors' experimental results and their interpretation. This primarily applies to the nature of the postulated ions.

Recently Reid [113] reported an interesting study of the absorption spectra of a number of aromatic hydrocarbons in a mixture of hydrogen fluoride and boron fluoride, i.e., in a system which can act as a very strong complex oxygen-free acid.

$$HF + BF_3 \rightleftarrows HBF_4 \rightleftarrows H^{+} + BF_4^{-} \qquad (108)$$

The spectra of all the monocyclic hydrocarbons studied (benzene, toluene, mesitylene, hexaethylbenzene) and of hydrocarbons with condensed aromatic nuclei (naphthalene, anthracene, phenanthrene, naphthacene, pyrene, fluoranthene) showed characteristic absorption bands attributed to carbonium ions. In some instances these bands coincide with the absorption bands described by Gold and Tye for sulfuric acid solutions, and they should be attributed to the same causes. The maximum for all the monocyclic hydrocarbons and for naphthalene and anthracene is about 4000 A. For the other hydrocarbons this maximum in HF-BF$_3$ solution is shifted into the long-wave direction, and lies in the 4800-5000 A region. On the basis of the work of Picket, Muller and Mulliken [114], Reid regards the carbonium ions in all cases as forms with excess H^{+}. They are $C_6H_7^{\oplus}$ for benzene, $C_7H_9^{\oplus}$ for toluene, $C_{10}H_9^{\oplus}$ for naphthalene, etc. In other words, Reid's carbonium ions contain 2 more H atoms than those of Kursanov, Otvos, Beeck and Gold. It should be noted that Reid's interpretation is based on the very sound theoretical analysis made by Mulliken and his associates, and is in better agreement with the donor properties of HBF$_4$. For such an acid the transfer of a proton to an aromatic hydrocarbon is more likely than the removal of a hydride ion H^{-} from it. According to Mulliken and Reid, a proton joins one carbon atom and forms a methylene group in hyperconjugation with the rest of the ring. If one ring interacts with the added H, the band is at about 4000 A. If two or more rings interact with the new electronic structure, the maximum is shifted to 4800-5000 A. The following structure is postulated for the anthracene carbonium ion ($C_{14}H_{11}^{\oplus}$), which gives an absorption band at about 4000 A.



Interesting conclusions are also drawn from the spectroscopic data concerning the mobility of the (+) charge within the ring which has added the H^{+}, and the possibility of displacement of H^{+} to adjacent rings. For example, in a system with two condensed rings, 9 centers and 8 electrons of the ring are involved in conjugation with CH$_2$ instead of five centers with four electrons; and in a hydrocarbon with three rings (phenanthrene), 13 centers and 12 electrons (not counting CH$_2$). It is interesting that for benzene and toluene, the most basic hydrocarbons in this group, the characteristic color of the carbonium ion does not appear at once. The carbonium ion is preceded by some other form with an absorption band at 2840 A for benzene, 3180 A for toluene, and 4000 A for xylene. Under the action of absorbed light the carbonium ions undergo further chemical changes, which are particularly rapid for pyrene. Reid considers that these are probably tautomeric changes of the carbonium ion induced by light. The electron transitions which occur on absorption of light, and the changes which follow these transitions, are shown schematically in Fig. 51.

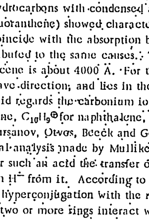


Fig. 51. Probable form of potential curves of the pyrene carbonium ion [114]. 1) Original carbonium ion; 2) excited state of carbonium ion; 3) curve representing the transition of 2 into the tautomeric form; 4) final state of the photochemical product.

A further contribution of our knowledge of ions formed by aromatic hydrocarbons has been made by Hum and Yu [115], who studied the magnetic susceptibility of hydrocarbon anions formed in solution by interaction with alkali metals. It has been known since the 1930's that alkali metals in certain solvents are capable of reacting with aromatic hydrocarbons with transfer of electrons to the hydrocarbons and formation of colored ions [116]. In Ingold's terminology, this is a nucleophilic process. Since sodium transfers electron to the hydrocarbon, The latter is reduced while the sodium is oxidized. For the transfer of one electron the process may be represented as follows:

$$Me + C_nH_m \rightarrow Me^{\oplus} + C_nH_m^{\ominus}. \tag{109}$$

Similar transitions of two electrons to one molecule are possible according to the scheme

$$2Me + C_nH_m \rightarrow 2Me^{\oplus} + C_n^{\ominus\ominus}H_m. \tag{110}$$

The physicochemical and energetic aspects of these reactions were recently discussed by Lipkin and others [116]. Hum and Yu [115] used anthracene, biphenyl, naphthalene, phenanthrene, and metaterphenyl in tetrahydrofuran solution. The reducing agent supplying electrons to the hydrocarbon was metallic sodium. Reduction of most of the hydrocarbons (anthracene, naphthalene, and others) to univalent (−) ions was rapid and complete. In the case of diphenyl a mobile equilibrium is established

$$Na + C_{12}H_{10} \rightleftarrows Na^{\oplus} + C_{12}H_{10}^{\ominus}. \tag{111}$$

Univalent anthracene and phenanthrene anions can be further reduced to the bivalent state, but the process is very slow at room temperatures. The bivalent ions were found to be diamagnetic. The univalent ions are paramagnetic, as free monoradicals should be. The values of paramagnetic susceptibility in various solutions indicate the absence of any appreciable dimerization of univalent anions, but in such solutions there is also a slow disproportionation process, accompanied by disappearance of paramagnetism. These results, in conjunction with earlier data, convincingly demonstrate the existence of anions with excess number of electrons and normal number of protons. Thus for C_nH_m hydrocarbons the existence of

$$[C_nH_{m+1}]^+,\ [C_nH_m]^- \text{ and } C_nH_m^{2-}$$

ions has been definitely proved, and the formation of $[C_nH_{m-1}]^+$, $[C_nH_{m+1}]^-$ and other ions is postulated.

It is possible that the true number of types of hydrocarbon ions met in ordinary chemical and isotopic exchange reactions is less, and that some of them are imaginary forms introduced ad hoc to explain definite groups of facts. A consequence of the contradictory views on the nature of the ions is the contradictory nature of the views on the mechanism of their formation. In most work on isotopic exchange and acid catalysis the condition for carbonium ion formation was preliminary incomplete oxidation of the original molecules. In the experiments of Lipkin, Paul et al. [116], and in the Hum and Yu investigation [115] which we have considered in detail, the ions were formed by reduction by means of very strong reducing agents. In most of the spectroscopic, cryoscopic, and conductometric studies the ions were formed without oxidation and reduction as the result of normal protolytic dissociation. There are also great differences in the views on the stability and reactivity of the hydrocarbon ions. Despite such contradictions, the sum of the experimental data on the physical and physicochemical properties of hydrocarbons dissolved in concentrated mineral acids is of great value for interpretation of the mechanism of the isotopic exchange of hydrogen in acid media. The results are difficult to explain without assuming direct or exchange dissociation of the dissolved molecules. For conclusive interpretation of the observed T_f depressions and changes in the absorption spectra as consequences of carbonium acid formation on dissociation, we lack quantitative electrochemical data on specific conductances of the solutions and on transference numbers. Studies of absorption spectra give the most direct indications of the presence of charged hydrocarbon ions in hydrocarbon solutions. Since such measurements are not of high sensitivity, if the authors' interpretation of the spectra is accepted, we must assume that in the systems in which deuterium exchange was studied, ions were formed in concentrations of the same order as the concentrations of the original hydrocarbons. This, however, is difficult to reconcile with the deuterium exchange and isomerization mechanisms postulated by most investigators.

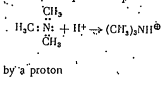
To explain the mechanism of chemical reactions of the acid–base type involving carbonium ions, the latter are assumed to have exceptional lability and chemical instability [117], and therefore their equilibrium contents cannot be high. It is evident that it would be rash to assume that the carbonium ions detected by spectroscopic and physicochemical methods are identical with the carbonium ions of Whittaker and his school. This applies with even greater force to the carbonium mechanism of isotopic exchange. The mechanism for the formation of super-equilibrium concentrations of polydeuterated molecules definitely requires a low absolute content of active forms, and their slow appearance and disappearance. There appear to be no other ways of explaining the high contents of multisubstituted deutero hydrocarbons in the experiments of Beeck and others. Consequently, the forms which effect the process could not be detected from freezing point depressions, magnetic susceptibilities, or absorption spectra in the conditions used by Gold, Reid, Lavrushin, and Hum and Yu, irrespective of whether these forms are electrically charged or neutral association or dissociation products. The appearance of new maxima, caused by active intermediate exchange products, in the absorption spectra is possible, but the intensity of such maxima would be negligible. Therefore it is probably incorrect to ascribe the maxima found, the intensity of which was of the same order as in sulfuric acid solutions of carbinols, to active intermediate isotopic exchange forms.

§17. The Electrophilic Nature of Hydrogen Exchange

The preceding sections contained an examination of the characteristics of isotopic hydrogen exchange in free organic radicals and organic carbonium ions. When these active forms are capable of being formed in appreciable concentrations, they can participate in isotopic exchange of the original stable molecules, acting as peculiar catalytic carriers. At the same time there are no doubts as to the possibility of hydrogen exchange effected by way of reversible protolytic dissociation of the exchanging molecules, and also exchange involving active tautomeric forms. However, these four types of mechanism do not cover the great diversity of phenomena observed in hydrogen exchange; and there are serious grounds for ascribing an independent role to bimolecular isotopic exchange proceeding through intermediate addition complexes, which do not fit into any of these categories. A.I. Brodsky [56], G.P. Miklukhin [57], and others consider that this type of exchange is predominant in organic compounds. A.I. Shatenshtein and his associates also ascribe an important role to this type. The classification of actual hydrogen exchange reactions in any of these types presents a difficult, and sometimes an insoluble problem, as, on one hand, there are continuous gradations between these types, and on the other, it is unlikely that they include all the mechanisms which operate in practice. It is therefore desirable to examine the mechanism of deuterium exchange from a more general standpoint.

The theory of nucleophilic and electrophilic reactions, which is a peculiar and very valuable combination of the electronic theory of oxidation and reduction with the electronic theory of acids and bases, has proved very fruitful in this respect.

In the most extreme typical cases, according to L.V. Pisarzhevsky [118], Lewis [119], and Steiglitz [120], the elementary act of oxidation is the loss of one or several electrons, and the elementary act of reduction is a corresponding gain. The basis for this interpretation of oxidation and reduction was already contained in the early work of Abegg [121] and Drude [122] on the electronic theory of negative and positive valence. This theory, which provided an elegant and simple explanation for the simplest oxidation–reduction reactions in solutions [123] and many photochemical [124] and radiochemical processes [125], met great difficulties in relation to the reactions of organic substances [126–128]. This made it necessary to extend the concept of oxidation and reduction also to acceptor–donor or coordination bond formation [119], when a covalent bond is formed by the addition of an acceptor atom or group with an incomplete number of electron pairs in the octet, to a free electron pair of a complete octet of another atom (the donor). The formation of such a bond with a pair of electrons entering the electron shells of two atoms linked by a covalent bond is oxidation with respect to the atom (or ion or group) of the donor, the octet of which contained a free electron pair before the reaction, and reduction with respect to the atom (or ion or group) of the acceptor with an incomplete octet, added to this electron pair. From this viewpoint, oxidation–reduction processes include any addition of halide ions or hydrogen ions, for example, addition of a fluoride ion to boron fluoride or of a proton to trimethylamine



$$:\ddot{F}:^{(-)} + \overset{F}{\underset{F}{\ddot{B}}}:F \rightarrow [F:\overset{F}{\underset{F}{\ddot{B}}}:]F^{(-)}$$

$$H_3C:\overset{CH_3}{\underset{CH_3}{\ddot{N}}}: + H^+ \rightarrow (CH_3)_3NH^{\oplus}$$

and even neutralization of a hydroxyl by a proton

$$H:\ddot{O}:^{(-)} + H^+ \rightarrow H:\ddot{O}:H$$

This last reaction, like the reversible reactions of other charged and neutral substances involving proton transfer, belongs to the class of protolytic reactions according to the theory of acids and bases advanced by Brønsted [126] and Lowry [127]. By this theory, in the schematic equation

$$B + H^+ \rightleftarrows A \qquad (112)$$

B is a base, and A is its conjugate acid; for example

$$\left.\begin{array}{l} \underset{\text{base}}{CN^-} + H^+ \rightleftarrows \underset{\text{acid}}{HCN} \\ \underset{\text{base}}{NH_3} + H^+ \rightleftarrows \underset{\text{acid}}{NH_4} \end{array}\right\} \qquad (112a)$$

Many authors (Lewis, Usanovich, and others [55, 128, 129, 130, 131]) have extended the concepts of acid and base, and included in them reactions involving transfers of other cations and anions, and all addition reactions in which free electron pairs are utilized. Many reactions which were formerly regarded as of the oxidation–reduction type were thereby included in the conjugate acid–base class.

This very broad interpretation of the concepts of oxidation and reduction, and of acids and bases, may be convenient in certain instances, but it has proved to be more effective to retain, for oxidation and reduction and for acids and bases, the old definitions with the addition of new and broader concepts, which include oxidation–reduction reactions with direct electron transfer and cation and anion transfers as extreme cases. These are the concepts of nucleophilic and electrophilic substances. Any reagent which gives its electrons to other atoms or shares them with other atoms in chemical reactions with coordinate bond formation, is known as a nucleophilic reagent, while any reagent which receives, in a chemical reaction, electrons from other atoms or partially utilizes electrons which were formerly completely included in the electron shells of other atoms, is known as an electrophilic reagent or electrophile.

TABLE 53

Nucleophile Reagents, after Ingold

Reagent	Number of active electrons (or pairs)	Participation of electrons in oxidation–reduction process	Note*
$[Fe(CN)_6]^{4-}$	1 electron	Complete transfer	R
$Na_{(met)}$	1 electron		R
Sn^{2+}	2 electrons		R
SO_2	1 pair	Enters compound by its pair	R
S^{2-}	1, 2, 3, 4 pairs		R, B
CN^-	1 pair		(R), B
OH^-	1, 2 pairs		B
NH_3	1 pair		B
$[Co(H_2O)_5(OH)]^{2+}$	1 pair		B

---

*R is a reducing agent in the pre-electronic sense; B is a base in the Bronsted–Lowry theory.

This division of reagents into the two above groups is not absolute. Some reagents can, according to conditions, act either as nucleophiles or as electrophiles. Nucleophilic and electrophilic reagents correspond to nucleophilic and electrophilic substitution, addition, and decomposition reactions. Nucleophilic substitution reactions, often denoted by S_N, include numerous reactions of organic halides with halide ions, organic sulfides, cyanide ions, substituted amines, etc. By the detailed balancing principle, all the reverse reactions proceed by the same mechanism but in a reverse stage sequence. Electrophilic substitution reactions, often denoted by S_E, include numerous reactions of aromatic hydrocarbons, amines, and alcohols with nitric acid; Hal^+ ions and free halogens, sulfuric acid, etc. The nature and distribution of these two classes of reactions can be illustrated by Table 54.

TABLE 54

Examples of Nucleophilic and Electrophilic Substitution Reactions, after Ingold

Reagent	Substrate	Substitution product
	Nucleophilic substitution reactions	
Hal^-	$Alk \cdot Hal^-$	$Alk\ Hal$
OR^-, OHR	$Alk \cdot Hal$	$Alk\ OR$
SR_2	$Alk \cdot Hal$	$Alk \cdot SR_2^+$
NHR_2	$Alk\ Hal$	$Alk\ NR_2$
NR_3	$Alk\ Hal$	$Alk\ NR_3^+$
CN^-	$Alk \cdot Hal$	$Alk\ CN$
$HHal$	$Alk \cdot OR$	$Alk\ Hal$
Hal^-	$Alk \cdot SR_2^+$, $Alk \cdot NR_3^+$ etc.	$Alk\ Hal$
OR^-, OHR	$Alk \cdot SR_2^+$, $Alk \cdot NR_3^+$ etc.	$Alk\ OR$
NR_3	$Alk \cdot SR_2^+$	$Alk\ NR_3^+$
$NOHal$	$Alk \cdot NH_2$	$Alk \cdot Hal$
$NOOR$	$Alk \cdot NH_2$	$Alk\ OR$
	Electrophilic substitution reactions	
NO_2^+, HNO_3 etc.	ArH, R_2NH, ROH	$ArNO_2$, $R_2N\ NO_2$, $RO\ NO_2$
Hal^+, Hal_2 etc.		$ArHal$, R_2NHal, $ROHal$
SO_3, H_2SO_4 etc.		$ArSO_3H$, R_2NSO_3H, $ROSO_3H$
RCO^+, $RCOCl$ etc.		$ArCOR$, R_2NCOR, $ROCOR$
$Ar' \cdot N_2^+$		ArN_2Ar', $R_2N\ N_2Ar'$, RON_2Ar
NO^+, HNO_2 etc.		$ArNO$, $R_2N\ NO$, $RONO$
Alk^+, $Alk \cdot Hal$ etc.		$ArAlk$, $R_2N\ Alk$, $RO\ Alk$

The electrophilic and nucleophilic concepts also proved very useful with regard to many addition and decomposition reactions; their applicability to intramolecular regroupings is debatable. These concepts have assisted the interpretation of the peculiar laws which determine the predominant directions and rates of substitution in organic compounds.

It has been shown by the work of numerous investigators, among which the studies carried out over many years by Flursheim [132] and Holleman [133] deserve special mention, the introduction of substituent groups into an aromatic ring may exert a dual orienting effect on subsequent substitution and addition reactions. Some substituent groups direct certain reactions predominantly to atoms in the ortho- and para-positions relative to the first substituent, and others, to the meta-position. Substituents which direct the processes to ortho and para atoms usually accelerate the processes, while substituents with a directing effect toward the meta atoms retard them. Further investigations revealed additional relationships which shed some light on the complex situation, and made it possible to develop electronic theories of orientation effects [134-138]. Thus, it was found that a positively charged ionic center directly linked to a benzene nucleus attracts a portion of the electron cloud of the benzene nucleus and lowers its electron density. This decreases the rate of nitration, which is directed to the meta-position. This effect is produced, in particular, by $PhNMe_3^+$, $PhPMe_3^+$, $PhSMe_2^+$, $PhHg^+$, $PhTl^+$, Ph_2Sn^{2+}, Ph_2I^+, and also by oxonium oxygen* [139]. This influence, which weakens with distance, is also transmitted to the aromatic nucleus through long chains. For example, NMe_3^+ directs nitration into the meta-position not only in $C_6H_5NMe_3$ but also in $C_6H_5CH_2NMe_2^+$ and even in $C_6H_5-CH_2-CH_2-CH_2-N^+Me_2^-$ [140]. With such a structure of the substituent, the predominance of electrostatic attraction of electrons results in a decrease of the effect as we pass from light to heavy elements in any one group of the periodic system. Hence the influence is in the following sequence

$$N^+ > P^+ > As^+ > Sb^+.$$

---

*In these compounds Ph is phenyl, C_6H_5; Me is methyl, CH_3.

For the same reason, orientation of a reaction toward the meta-position is weakened from right to left within each period of the periodic system [141, 142].

$$S^+ > P^+ \text{ and } Se^+ > As^+.$$

A similar influence to that of (+) ions is exerted by polar groups with (+) charges directed toward the ring, for example, the nitro group $^+NO_2^-$ and the sulfo group $^+SO_3^-R$ and $^+SO_3^-H$, and also neutral substituents, atoms and radicals with high affinity for electrons, such as Cl, Br, COR, CN; and H. Conversely, the ordinary alkyl radicals: CH_3, C_2H_5, etc., and also O⁻, NR_2^-, OR⁻ exert the opposite directing effect, repelling electrons and directing the reaction into the ortho-position.

The physical nature of such orientation and the origins of a number of complex and peculiar relationships found when a nucleus contains two or more substituents (of the same or of different classes) are examined very fully and in detail by Ingold in his monograph [60].

All the above relationships are valid for reactions of electrophilic substitution of hydrogen in the benzene nucleus, which include, in addition to nitration, also halogenation (chlorination, bromination, iodination), diazotization, mercuration, acetylation, etc. In all these cases, to explain the observed facts, it is often assumed that positively charged forms with incomplete numbers of electrons are first formed; for example, nitronium $(NO_2)^+$ in nitration, chloronium Cl^+ or its hydrate $ClOH_2^+$ in chlorination, ArN_2^+ in diazotization. This mechanism has not been proved for every case, but there are very serious grounds for considering the participation of charged or neutral electrophiles (as defined on page 180) a necessary condition for the characteristic features of aromatic substitution.

Early investigations of deuterium exchange of aromatic hydrocarbons with water and acids indicated that this substitution reaction is of an electrophilic character, with respect to which the sequence of deutero substituents coincides with the sequence of acids in order of diminishing strength [143]

$$D_2SO_4 > D_2SeO_4 > D_3O^+ > PhOD > D_2O.$$

This conclusion was confirmed after systematic investigations of deuterium exchange in aromatic compounds. For example, Kharash et al. [143] and Best and Wilson [94], established that only three H atoms, situated in the ortho- and para-positions, are exchanged at moderate temperatures in aniline and dimethylaniline with deuterium oxide or deuteroalcohol DOC_2D_5, acidified with hydrochloric acid. As in ordinary chemical substitution reactions, in these deuterium exchange reactions the electronegative (basic) substituents [NH_2 and $N(CH_3)_2$] accelerated isotopic exchange, which occurred, other conditions being equal, much more rapidly than in benzene, and mainly in the ortho- and para-positions. In accordance with the general laws of electrophilic exchange in the aromatic nucleus, the introduction of a sulfo group, which is an electropositive substituent, has the opposite effect: it retards exchange so much that it does not proceed even with concentrated deuterosulfuric acid [92]. With weaker effects of the same kind it is possible to prove the existence of slow exchange localized at the meta carbon atoms.

There has been no lack of attempts to extend the concept of the electrophilic nature of deuterium exchange to other classes of hydrocarbons and to compounds of other chemical functions [144]. Arguments against such universal application of electrophilic mechanisms were provided by isolated observed instances of rapid acceleration of deuterium exchange by alkalies, which are typical nucleophiles. For example, D_2 and certain hydrocarbons exchange with water in alkaline solutions.

§18. The Acid-Base Concept of the Hydrogen Exchange of Hydrocarbons

The concept of an acid–base protolytic mechanism of deuterium exchange, developed in recent years mainly by A.I. Shatenshtein and his associates, has proved more flexible. As was stated at the beginning of the previous section, the concept of electrophilicity has combined the concepts of oxidizing power and acidity. In the same way, nucleophilicity represents a peculiar synthesis of the concepts of reducing power and basicity. These generalized ideas have proved very productive in the kinetics of organic reactions and have been widely adopted. However, this resulted in the loss of the quantitative character of the concepts of oxidizing and reducing power and acidic and basic properties in the chemistry of solutions and in electrochemistry [55, 145-147]. Oxidation–reduction reactions, in the chemical sense of the term, do not play any significant role in the isotopic exchange of hydrogen. This makes it definitely more advantageous to discuss isotopic exchange in the light of the narrower and more definite protolytic theory of acids and bases; the electrophilic and nucleophilic theory is used only in consideration of individual more complex effects.

The basis of the Bronsted–Lowry protolytic theory of acids and bases is the existence of mobile equilibria of proton transfer between conjugate acid–base pairs (A and B, A' and B', etc.). Both A and B may be positively charged, neutral, or negatively charged particles.

$$\left.\begin{array}{l} \underset{\text{acid}}{A} \rightleftarrows H^+ + \underset{\text{base}}{B} \\ \underset{\text{acid}}{A'} \rightleftarrows H^+ + \underset{\text{base}}{B'} \end{array}\right\} \qquad (113)$$

A and B may be molecules of dissolved substances, solvent molecules, and various products of their interaction in solutions. By this theory there are no substances which always and in all cases react only as acids or only as bases. For almost every substance X it is possible to find substances C with a lower affinity for protons than X, and substances D with a higher affinity for protons than X. X will have the function of a base with respect to the former, and of an acid with respect to the latter

$$\left.\begin{array}{l} C + X \rightleftarrows B^- + XH^+, \\ D + X \rightleftarrows DH^+ + Y^-, \end{array}\right\} \qquad (114)$$
$$A_X \xleftarrow{+H^+} X \xrightarrow{-H^+} B_X,$$

where A_X is XH^+ and B_X is Y^-.

The nature of the predominant acidic or basic function of a given substance depends greatly on the solvent. In basic solvents such as liquid ammonia, the molecules of which have a higher affinity for protons than do water molecules, many substances which act as bases in aqueous solutions have acidic properties. At the same time, the range of substances which exhibit basic properties diminishes in basic solvents, and distinctions between them tend to diminish. The opposite situation is found in acid solvents the molecules of which have a lower affinity than water for protons. Examples of such solvents are liquid hydrogen halides (HF, HCl). The range of substances functioning as bases increases and the range of substances with acidic properties decreases in acid solvents.

Prior to the work of Shatenshtein, isotopic exchange of hydrocarbons had been studied primarily in aqueous solutions and in solutions of acids capable of side chemical reactions with hydrocarbons (H_2SO_4, H_2SeO_4). Alcoholic solutions were used less often. Shatenshtein was the first to show the possibility, for many organic compounds, of effecting hydrogen exchange in liquid deuteroammonia, studied this exchange in great detail, and found that the alkali metal amides are powerful catalysts for it [148-150]. An understanding of the mechanism of hydrogen exchange was greatly assisted by a systematic comparison of hydrogen exchange in deuteroammonia as a typical strongly basic solvent, and liquid deuterium bromide as a strongly acidic solvent. The principal results obtained up to 1952 are considered in a review [151] published in "Uspekhi Khimii" (Progress of Chemistry). This review and the subsequent publications of 1953-1955 [152-154] convincingly prove the existence of at least two fundamentally different deuterium exchange mechanisms in hydrocarbons. The first, analogous to the Ingold and Boenhoeffer electrophilic mechanism, is typical for strong acid solvents and was studied in detail for exchange in deuterium bromide. All hydrocarbons exchanging in this solvent behave as weak bases. According to the data in this series of papers, the process begins by addition of a deuteron to hydrocarbon, in the particular case of naphthalene, $C_{10}H_8D^+$ is formed

$$C_{10}H_8 + DBr \rightleftarrows [C_{10}H_8D]^+ + Br^-. \qquad (115)$$

Subsequently the $C_{10}H_8D^+$ ion decomposes, releasing a proton

$$[C_{10}H_8D]^+ \rightleftarrows C_{10}H_7D + H^+. \qquad (116)$$

or, in the aggregate,

$$C_{10}H_8 + DBr \rightarrow C_{10}H_7D + HBr. \tag{117}$$

It is evident from Equations (115) and (116) that the primary addition product is identical with the aromatic complex of Reid [113] and others. Shatenshtein does not consider the existence of RHD^+ cations in the free state essential. In some instances the process may involve free ions, and in others it may occur within ionized associated molecules

$$C_{10}H_8 + DBr \rightleftharpoons [C_{10}H_8D]^+Br^- \rightleftharpoons C_{10}H_7D + HBr, \tag{118}$$

which may be similar to intermediate complexes. In such a case the activation energy would coincide with the heat of formation of the endothermic ionized complex $C_{10}H_8D^+Br^-$, which we will denote by $E = Q_{+-}$, while the rate would be calculated from the usual equations on the intermediate state theory. Another variation is possible, in which the slow determining stage is formation of RHD^+, or $RHD^+ + Br^-$, with the properties of ordinary ions or polar molecules. In such a case there may be an activation barrier between RH and RHD^+, and the experimentally determined E corresponds to some other intermediate complex and does not coincide with Q_{+-}.

According to this scheme, the stronger the deutero acid, the more rapid the exchange should be. The strongest of the known deutero acids, $D_2S_2O_7$ and $DClO_4$ [155] are inconvenient to use, being powerful oxidants which form side products with hydrocarbons even on mild heating. A strong acid, with a dissociation constant higher than that of DBr, may be obtained by dissolving in DBr aluminum bromide and other metal halide molecules which have the properties of protonic acids. Indeed, according to Klitz and Langseth [156] $AlBr_3$ accelerates deuterium exchange in hydrocarbons dissolved in deuterium bromide, and the exchange becomes appreciable even in hydrocarbons which practically do not exchange in pure DBr, such as cyclohexane [157]. This can be attributed to the action of the complex $DAlBr_4$, which would be a very strong acid; however, its formation according to Equation (119) is very doubtful [158].

$$AlBr_3 + DBr \rightleftharpoons DAlBr_4 \rightleftharpoons D^+ + AlBr_4^-. \tag{119}$$

Therefore it is better to write the equation for the exchange without separation of the stages, as a reaction between the three substances RH, DBr, and $AlBr_3$

$$RH + DBr + AlBr_3 \rightleftharpoons RHD^+AlBr_4^- \rightleftharpoons RD + HBr + AlBr_3. \tag{120}$$

Such exchange schemes are close to Ingold's electrophilic substitution schemes, and all the factors which increase the electron cloud density in the hydrocarbon should intensify the exchange, directing it toward regions of maximum electron density in the chain or ring. In this interpretation there is no formation of carbonium ions, which, according to Kursanov, Voevodsky, and some American authors, constitute the main intermediate active forms in the exchange.

According to Shatenshtein, exchange in basic solvents is quite different in character. Deuteroammonia, owing to the presence of a free electron pair, is a nucleophile and a base with a high proton affinity. Basic and nucleophilic properties are still stronger in alkali metal amides, which are soluble in ammonia and which partly dissociate into Me^+ and NH_2^-. Therefore exchange in liquid ammonia begins with the removal of the most acid proton from a C atom of the hydrocarbon. The result is a negatively charged anion, a carbanion R^-, such as $C_6H_5^-$ from benzene or $C_{10}H_7^-$ from naphthalene.* Proton-removing reagents in liquid ammonia are deuteroammonia molecules ND_3 and amide ions formed by protolytic dissociation of ammonia

$$ND_3 + ND_3 \rightleftharpoons ND_4^+ + ND_2^-, \tag{121}$$

and, in considerably greater concentrations, from metal amides:

$$MeNH_2 \rightleftharpoons Me^+ + NH_2^-. \tag{122}$$

*It should be emphasized that Shatenshtein's hydrocarbon anions such as $C_6H_5^-$ with a vacant electron pair and a deficiency of H^+ differ sharply from hydrocarbon anions of the type $H_6C_6^-$, formed by the action of alkali metals on aromatic hydrocarbons.

The exchange as a whole may be represented as proceeding with the formation of free "carbanium" ions.

$$\left.\begin{array}{r} RH + ND_3 \rightarrow R^- + ND_3H^+; \\ R^- + ND_3H^+ \rightarrow RD + ND_2H; \\ RH + NH_2^- \rightarrow R^- + NH_3; \\ R^- + ND_3 \rightarrow RD + ND_2^- \end{array}\right\} \tag{123}$$

or molecular amine ions

$$RH + ND_2^- \rightleftharpoons R^-(HND_2) \rightleftharpoons RD + NHD^-. \tag{124}$$

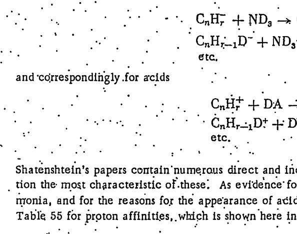


Fig. 52. Schematic variation of exchange rate with the acid–base properties of the solvent. To left of pH_{H_2O} – region of action of electrophilic acid solvents; to right – of nucleophilic basic solvents.

In this interpretation, the exchange is a nucleophilic process. Its laws differ sharply from the laws of electrophilic exchange, and to some extent contrary to the latter in the influence of chemical factors, orienting effects, etc. In particular, the exchange should be intensified with decreasing electron cloud density, and should be directed toward the carbon atoms with minimum electron densities. Convincing evidence for this is the very fact of the catalytic action of metal amides. It is also supported by the nature of the influence of substituents on the rate and direction of the exchange, and by the parallelism between the series formed by the hydrocarbons and solvents in order of diminishing exchange rates and in order of decreasing basicity. The dependence of exchange rates on the acid–base properties of the solvent can be schematically represented by the diagram in Fig. 52. As in deuterium exchange with acid, the nature of the determining stage is not yet clear. In the light of the data of Otvos, Wagner, *et al.* and of Voevodsky, it is possible that the consecutive exchange proceeds not by an addition–decomposition scheme, but by a double decomposition scheme

$$\left.\begin{array}{l} C_nH_r^- + ND_3 \rightarrow C_nH_{r-1}D^- + ND_2H; \\ C_nH_{r-1}D^- + ND_3 \rightarrow C_nH_{r-2}D_2^- + ND_2H \\ \text{etc.} \end{array}\right\} \tag{125}$$

and correspondingly for acids

$$\left.\begin{array}{l} C_nH_r^+ + DA \rightarrow C_nH_{r-1}D^+ + HA; \\ C_nH_{r-1}D^+ + DA \rightarrow C_nH_{r-2}D^+ + HA \\ \text{etc.} \end{array}\right\} \tag{126}$$

Shatenshtein's papers contain numerous direct and indirect data which confirm this interpretation; we will mention the most characteristic of these. As evidence for the increased exchange capacity of hydrocarbons in ammonia, and for the reasons for the appearance of acid properties in the process, there is given the interesting Table 55 for proton affinities, which is shown here in somewhat modified form.

This table explains very convincingly the different behavior of water and ammonia, and the catalytic effects of dissolved hydroxides and alkali metal amides. Data on the electrical conductivity of hydrocarbons in ammonia and hydrogen halides which show the formation, in the first case, of negative carbanions such as the $(C_6H_5)_3C^\ominus$ from triphenylmethane $(C_6H_5)_3CH$, and in the second case, of positive ions, are instructive. In this connection we refer to the data of Gold *et al.* [111, 112] on the absorption spectra and cryoscopic behavior of hydrocarbons dissolved in sulfuric acid, which led them to postulate the formation of carbonium cations in this solvent

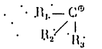


TABLE 55

Proton Affinity Energy, after K.B. Yatsimirsky

Substance	Reaction	Heat of reaction kcal/mole
Water	$H_2O + H^+ \rightarrow H_3O^+$	180
Ammonia	$NH_3 + H^+ \rightarrow NH_4^+$	214
Hydroxyl ion . .	$OH^- + H^+ \rightarrow H_2O$	383
Amide ion	$NH_2^- + H^+ \rightarrow NH_3$	419

The chemical reactions of hydrocarbons also clearly show their acidic and basic properties. For unsaturated compounds they are seen in the possibility of direct substitution of hydrogen by metals, particularly characteristic for acetylene and its derivatives, which are typical weak protonic acids. Silver and copper acetylides, calcium carbide, and similar compounds are salts which may be formed from acetylene by direct displacement of hydrogen by metals. In their lattices carbon is present as C_2^{2-} anions, and metals as Me^{2+} [158]. However, carbides which are derivatives of ethylene or even of methane are well known, such as Al_4C_3. A.I. Rabinovich, V.A. Kargin and F.V. Fodiman [159], using the method proposed by A.I. Shalnikov and myself for the preparation of alkali metal organosols by condensation of vapors of these metals with solvent vapors on surfaces cooled by liquid air [160], found that, when a potassium organosol is unfrozen in benzene, free hydrogen is evolved, as the result of displacement of H by K. The acid properties of hydrocarbons are very clearly demonstrated in the metallization of hydrocarbons, described by P.P. Shorygin [161], and developed further by many others, including K.A. Kocheshkov and T.V. Talalaeva [162, 163]. This reaction consists of simple displacement of a weaker by a stronger acid, for example, of ethane by benzene

$$C_6H_6 + C_2H_5K \rightarrow C_6H_5K + C_2H_6. \qquad (127).$$

American authors have used this reaction to construct an acidity scale [165], quoted from McEven in Table 56.

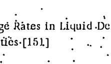
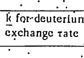
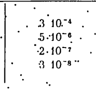
In this scale the ionization constant for methyl alcohol is taken as 10^{-16} and all the others are calculated in reference to this. There has been no lack of attempts at a quantitative evaluation of the basicities of hydrocarbons, from the solubility of hydrogen chloride in them, from distribution coefficients between strongly acid solvents and hydrocarbon solvents, etc. The combined results leave no doubt that any hydrocarbon can act as a base in a sufficiently acid medium, and as a acid in a sufficiently basic medium, and that there are very wide ranges of acidity and basicity among the hydrocarbons.

The work of Shatenshtein and his associates convincingly demonstrates the existence of a parallelism between deuterium exchange rate and acid–base properties. Table 57, quoted from Shatenshtein, gives the isotopic exchange rate constants for some of the hydrocarbons shown in the acidity table.

Table 57 clearly shows that the rate constant decreases with diminishing acidity. An increase of pK by 4 units (indene, fluorene) at 25°C produces a 160-fold decrease in the rate constant. At 120°C (triphenylmethane, diphenylmethane) a decrease of 2 units in pK produces a 10-fold decrease of k. The effect is so strong that, in order to make measurement of deuterium exchange possible, on passing from fluorene with pK = 25 to triphenylmethane with pK = 33 it was necessary to raise the temperature by nearly 100°, and despite this k is higher for fluorene than for triphenylmethane. At any one temperature the whole range of k in the transition from pK = 21 to pK = 35 would cover not less than 10^7 (!). It is evident that, with this very great influence of acidity, it is practically impossible to measure exchange in toluene, which is even more basic than diphenylmethane, without the use of a catalyst–carrier (KNH_2), while in the case of ethane it could not be measured even with a catalyst.

TABLE 56

Table of Hydrocarbon Activities, after McEven

Substance	Formula	Structure	Ionization constant pK = = −log k
Methyl alcohol*	CH_3OH	—	16*
Acetophenone	$C_6H_5COC_2H_5$		19
Indene	C_9H_8		21
Fluorene	$C_{13}H_{10}$		25
Triphenylmethane	$C_{19}H_{16}$	$(C_6H_5)_3CH$	33
Diphenylmethane	$C_{13}H_{12}$	$(C_6H_5)_2CH_2$	35
Cumene	C_9H_{12}	iso-C_3H_7 C_6H_5	37
Ethane	C_2H_6	$CH_3—CH_3$	>37

*Methyl alcohol is the reference substance.

TABLE 57

Comparison of Deuterium Exchange Rates in Liquid Deuteroammonia with Hydrocarbon Acidities [151]

Hydrocarbon	T, °C	k for deuterium exchange rate	pK
Indene	25	$3 \cdot 10^{-4}$	21
Fluorene	25	$5 \cdot 10^{-6}$	25
Triphenylmethane . .	120	$2 \cdot 10^{-7}$	33
Diphenylmethane . .	120	$3 \cdot 10^{-8}$	35

Extensive additional data confirming the validity of the interpretation of hydrogen exchange in hydrocarbons as an acid–base protolytic process can be found in Shatenshtein's review, which appeared after this monograph went to the press [164].

§19. Contradictions in Views on the Mechanism of Deuterium Exchange, Their Origins, and Attempts to Remove Them

Deuterium exchange has been studied more than any other type of isotopic exchange, and it clearly demonstrates the strong and weak aspects of modern isotopic exchange theories. As was shown earlier, studies of deuterium exchange revealed the existence of several chemical mechanisms of hydrogen atom exchange, by homolytic dissociation into atoms and by heterolytic dissociation into ions, with and without continuation by a chain mechanism. The important role of the usual types of tautomeric transformations and other types of isomerization in isotopic exchange has been proved. The nucleophilic character of exchange in alkaline media and the electrophilic character in acid media has been demonstrated, and it has been shown that the laws governing the influence of substituents and directing effects in nucleophilic and electrophilic substitution in organic chemistry are obeyed. Anomalies of isotopic composition have been found in isotopic exchange in gases and solutions, in-

[illegible] the participation of chemically labile intermediate forms, present in small concentrations, in the exchange. It [illegible] shown that exchange is accelerated if the exchanging atoms contain unpaired electrons (radicals) and free electron pairs (donors), or have incomplete electron shells. Relationships have been established between the rate of isotopic exchange and the chemical structure of hydrocarbons; exchange has been shown to be localized at definite reactive exchange centers (tertiary atoms, double bonds, etc.); and it has been shown that mechanisms exist for drawing hydrogen atoms, not directly linked to such active centers, into the exchange. The importance of catalytic transfer in isotopic exchange has been elucidated and the existence of several types of catalysis has been demonstrated. The mechanism for the acceleration of exchange by light and electric discharges has been clarified.

At the same time, a considerable number of contradictions and facts which are difficult to explain have accumulated. This refers primarily to the nature of the intermediate active molecules in the isotopic exchange of [illegible]. Most authors consider them to be ions, in some cases (+) and in others (−) ions. However, different configurations have been ascribed in different papers to the ions from the same compounds (principally hydrocarbons). For example, in the case of toluene some authors assume the cation to be $C_6H_5CH_2^{\oplus}$ with trivalent carbon and an electron sextet $Ph : \underset{H}{\overset{\oplus}{C}} : H$; others, $C_6H_5CH_3^{\oplus}$, and yet others $C_6H_5CH_3H^{\oplus}$. Toluene anions have been represented as $C_6H_5CH_3^{\ominus}$ and $C_6H_5CH_2^{\ominus}$, in different papers. The assumptions made concerning the properties of the ions are also difficult to reconcile. According to some authors, they are completely stable free ions conforming to the electrolytic dissociation theory, present in very high concentrations, strongly influencing the melting and boiling points, and easily detected from data on electrical conductivity, absorption spectra, and magnetic susceptibility. Others consider that the ions through which the exchange takes place are very rare formations, which occur in very slight concentrations. Others claim that the free ion model is not a legitimate representation of the effect, and that in reality electron transfer is confined to polarization with formation of hybrid covalent-ionic bonds. The questions of the nature of the determining stages for various typical cases, and of the quantitative characteristics of isotopic exchange, still remain obscure. Recently one prominent worker on deuterium exchange, A.I. Brodsky, has made an attempt to eliminate the existing contradictions by dividing all deuterium exchange reactions into rapid and slow, and basing his explanation of the observed differences in the rates on the presence or absence of free electron pairs. We give here an extract from this paper, which puts forward the fundamental principle of the new classification and gives the arguments in its favor [56].

"In their capacity for hydrogen exchange in solutions, the numerous compounds studied [50, 166, 167] form two sharply distinct groups. In the first, exchange is practically instantaneous at any temperature, and does not require catalysts. Exchange occurs in this way in N − H, O − H, S − H, Cl − H etc., bonds of most, although not all, compounds with acid-base deuterium donors such as D_2O, C_2H_5OD. This type of exchange we shall term rapid. In the second group of compounds exchange either does not proceed at all or is more or less slow. Its possibility and rate are determined by the structure of the molecules, the nature of substituents present in them, the reaction of the medium, and the properties of the deuterium donor. Exchange of this type, which we shall term slow, depends greatly on the temperature and on the presence of protolytic reaction catalysts. Slow exchange is characteristic for C − H bonds in organic compounds. The table shows that the type of exchange is not determined by the properties of the individual bonds in which the exchange occurs, or the nature of the atom directly linked to the exchanging hydrogen atom. In particular, despite the widely accepted view, it is not characterized by the polarization energy or the 'ionic fraction' of the bond . . ."

". . . The rapid or slow type of exchange in a bond of type X − H is determined by the presence or absence of free (unsaturated) electron pairs at the atom X. If these are present, then a deuteron (or proton) can be added to one of them with a simultaneous removal of a proton from another electron pair holding it . . ." This process does not require any considerable activation energy. ". . . Therefore the exchange proceeds very rapidly even at low temperatures. In the absence of a free electron pair, as in C − H bonds in organic compounds, a deuteron can only become attached to an electron pair which held a proton, after removal of the latter. This process requires a considerable activation energy, and the exchange proceeds slowly or not at all . . ."

". . . To confirm these views, some new examples of hydrogen exchange have been studied in our laboratory. There are no free electron pairs at the silicon atoms in Si − H bonds of organosilicon compounds, and no hydrogen exchange occurs in them. The work of I.G. Haskin and the author [168, 169] has shown the absence of exchange of triethyl-, triphenyl-, and triethoxysilane, $(C_2H_5)_3SiH$, $(C_6H_5)_3SiH$, and $(C_2H_5O)_3SiH$ with D_2O, C_2H_5OD and $(CH_3)_2ND$ even on prolonged heating above 100°. This result could not have been foreseen by analogy with exchange in the corresponding tertiary carbon compounds, as Si − H and C − H bonds differ very greatly not only in stability, but in the sign of polarization [170]. No signs of retarded exchange were found in ammonia, or in various amines and amides [171, 172] with free electron pairs at the nitrogen atoms, but exchange in the ammonium ion has measurable kinetics and proceeds in the course of hydrolysis involving ammonia. This is confirmed by the relationship, found by L.V. Sulima and the author [173] between the exchange rate in ammonium salts and the presence of concentrated strong acids which suppress hydrolysis. A similar mechanism governs slow exchange in $Co : NH_3$, $Pt : NH_3$, and $Pd \cdot NH_3$ in a number of hexammines and tetrammines, the kinetics of which greatly depends on the solution pH [50]. . ."

". . . According to literature data [50], gaseous H_2 does not exchange hydrogen with deuterium from heavy water in absence of catalysts which assist decomposition of H : H molecules. Exchange also does not occur in B − H bonds of borohydrides lacking free electron pairs at the boron atoms; it does not occur between BH_4^- and D_2O [174] or between $B_2H_6ND_3$ and liquid ND_3." The cases of slow hydrogen exchange which are now known are characterized by absence of free electron pairs at the atoms to which the exchanging hydrogen atoms are attached. " . . . On the other hand, no case is known* in which exchange does not occur very rapidly if such pairs are present. This gives grounds for considering that the views advanced here are well founded."

The basic idea of A.I. Brodsky's theory is fruitful and makes it possible to understand the extensive experimental material available on hydrogen exchange, and the empirical relationships found by other scientists. There are certain objections to the categorical contrast between rapid and slow exchange, and to the complete rejection of the widely held view, formerly supported by the same author [50] concerning the important role of electrolytic dissociation in rapid isotopic exchange. In the new interpretation, hydrogen exchange between $\ddot{X}H$ and $\ddot{Y}D$ molecules, both with spare electron pairs, is effected in a single elementary step through an intermediate state with a hydrogen bond

$$\ddot{X}H + D\ddot{Y} = \underset{\text{I}}{\begin{matrix} \uparrow X - H \downarrow \\ D - \ddot{Y} \end{matrix}} = \ddot{X}D + \ddot{Y}H \qquad (128)$$

The intermediate form I cannot be stable, if only because the presence of the X : D bond leaves no electrons for the D − Y bond, and the presence of the Y : H bond makes the simultaneous existence of X − H impossible. Therefore I is a particular instance of an intermediate collision complex. In order that exchange should proceed through I "practically instantaneously at any temperature, without catalysts," with complete reversibility of the isotopic exchange, the energy of formation of the complex I, $\Delta H \approx E$, should be practically zero, while the entropy should be greater or, at least, cannot be considerably lower than the entropy of the separate $\ddot{X}H$ and $\ddot{Y}D$ molecules. The second requirement is unlikely to be fulfilled, as the high structural symmetry of I, stressed by Brodsky, corresponds in the molecular kinetic collision theory to strict collision orientation, and in the statistical theory of intermediate complexes to a decrease in the number of rotational degrees of freedom, with a consequent decrease of entropy. Therefore the steric factor δ should be very small

$$\delta \ll 1. \qquad (129)$$

The author does not explain why $E \approx 0$. The analogy with the transference mechanism at anomalous conductivities, according to the Grotthus theory, with $E \sim 2$-3 kcal/mole can hardly serve as proof of the smallness of E. Therefore the reason for the rapidity of the exchange in all cases when $\ddot{X}$ and $\ddot{Y}$ have spare electron pairs remains obscure. We may note in this connection that, according to N.N. Semenov, processes which occur through plane intermediate complexes of the type of I do not play any significant role in kinetics, and linear complexes predominate. For isotopic exchange of the "slow type" by way of electrolytic dissociation, Brodsky postulates a stage reaction scheme involving a linear complex

$$YD + XH + YD \rightarrow YD\cdots X^{\ominus}\underset{H}{\cdots}H^{\oplus}\cdots YD \rightleftarrows YDX^{\ominus} + HYD^{\oplus} \qquad (130)$$

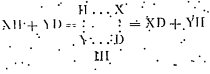
---

*Apart from a reference to retarded exchange between gaseous PH_3 and liquid H_2O, the kinetics of which may be determined by diffusion of the sparingly soluble phosphine into the solution [175].

[illegible] that this process requires considerable energy to split the X − H bond. In consequence E is small only when the expenditure of energy for splitting the X − H bond is compensated by solvation.

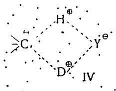
We cannot agree completely with A.I. Brodsky's view on rapid deuterium exchange, for the following reasons: 1) neither the theoretical arguments advanced in favor of Scheme (128), nor experimental data on rapid exchange in weak acids, exclude rapid exchange through ionization, but only show that it is unwise to assume that this mechanism is universal; 2) It is not clear whether the mechanism represented by (128) can ensure the required rates, or why it must be universal. It is well known that there are very considerable differences between the electron pairs in their ability to participate in formation of acceptor – donor bonds, and in many elements these pairs only enter the process with difficulty; 3) while in solutions slow deuterium exchange in presence of [illegible] pairs is met rarely (although not only in the exchange of PH_3 with water), in the gas phase a fairly considerable proportion of reactions of this type occurs slowly; for example, the exchange of F_2 with HF [176] or of ND_3 [illegible], while according to Scheme (128) the solvent molecules do not take part, and this retardation of exchange in gases should rather be an argument in favor of the dissociation mechanism; 4) the juxtaposition of rapid and slow reactions in solutions is itself artificial. It is very probable that, with suitable measurement techniques, appreciable values of E will be found for many rapid reactions, and an extensive gradation of rates will be found without a sharp distinction between rapid and slow reactions. Finally, some examples were given above of rapid exchange of hydrogen at low temperatures in unsaturated and aromatic hydrocarbons which do not contain free electron pairs in their molecules and which therefore cannot form complexes of the type postulated by A.I. Brodsky for typical rapid exchange reactions.

A.I. Brodsky's view on the mechanism of "slow exchange" do not essentially differ from those of other authors. In some instances it is an ionization mechanism, rejected for rapid exchange, and in others, an association mechanism, represented by the schemes

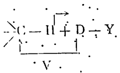


$$XH + YD \rightleftharpoons \underset{\text{III}}{\begin{matrix} H \cdots X \\ \vdots \qquad \vdots \\ Y \cdots D \end{matrix}} \rightleftharpoons XD + YH \qquad (131)$$

Assuming electrophilicity which the author, in contrast to Shatenshtein, regards as a general property of deuterium [illegible], the intermediate complex is assumed to have polarity

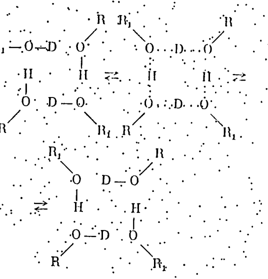

IV

or a substitution mechanism involving a third molecule, not shown directly in the scheme


V

is also considered. Because of the absence of free electron pairs, the complexes III, IV, and V are probably formed by hydrogen bonds. Without polarization and solvation this would make them highly endothermic with high values of E. Some of the objections would disappear if the terms "rapid" and "slow" exchange were abandoned. The theory would only benefit from this.

A.I. Brodsky's criticism of ionic mechanisms for rapid exchange has recently received support in the interesting paper by Kwart, Kuhn and Bannister [177] on deuterium exchange of methyl alcohol with water vapor. Because of the direct spectroscopic method used for studying the reactions by the intensities of the corresponding absorption bands in the near infrared, the numerical data are trustworthy. The authors showed that Jungers and Bonhoeffer [178] were right in the old controversy concerning the exchange rates. The hydroxyl hydrogen exchange is very rapid [175]. A new result was the rapid exchange in the gas phase, where total ionization is most improbable. It is interesting that various alcohols exchange their hydroxyl hydrogen with each other equally rapidly. The authors postulate, in explanation, the following "square" model of an intermediate exchange complex with tetramer formation:



through the agency of hydrogen bonds. These are increasingly used in recent times in explanations of the special features of hydrogen exchange [179].

We shall not consider here Brodsky's detailed discussion of the ionization mechanism, which is not directly related to the question under consideration. A.I. Brodsky's classification and the hypotheses of the rapid and slow exchange mechanisms on which it is based deserve verification and development, but his work eliminates only some of the difficulties and contradictions detailed at the beginning of this section.

It is probable that the origin of some of these contradictions lies in the methods used for the investigations. Qualitative rate characteristics predominate in the kinetics of isotopic exchange. At best, the rate is evaluated from the half-exchange time for one or two fortuitous combinations of conditions. Much would be clarified even by a mere transition to quantitative kinetic characteristics, with data on true reaction orders, rate constants, and activation energies and entropies for the processes. The experience of the development of studies of isotopic exchange with an electronic mechanism shows that the conclusive nature of the findings would more than compensate for the decrease in the number of systems studied, which is inevitable in a transition to quantitative characteristics. Quantitative kinetic investigations in flow systems, with application of modern methods for studying rapid processes, should make it possible to measure the rates and kinetics of many reactions which are at present considered as being instantaneous. For many of them the activation energies will also be found appreciable, $E \gg RT$.

§ 20. Mechanisms of Oxygen Exchange

In the preceding sections we have considered the mechanisms of isotopic exchange of elements the atoms of which are positively charged in their most typical compounds. This applies to metals in solvates with neutral molecules, their complexes with molecules and ions of either sign, and also to hydrogen, which is transferred mainly in the form of positive ions. In this and subsequent sections, with oxygen and the halogens as examples, we shall consider the characteristics of isotopic exchange of electronegative elements, for which negative ions are most typical in solutions. In covalent bonds, atoms of these elements are usually negatively polarized,

a) General characteristics of oxygen exchange

In contrast to hydrogen, which is most often transferred in the form of positive H^+, D^+, and T^+ ions, and which yields mainly positively charged solvates – $(H_3O)^+$, $(ND_4)^+$, $(CH_3CH_2OHT)^+$, oxygen forms practically only negatively charged ions. This is determined primarily by the characteristic distinctions in the ionization energies and electron affinities of these two elements, shown in Table 58.

This does not exclude the possibility of transfer of O^{18} and O^{17} in large anions – SO_4^{2-}, ClO_4^-, etc., or in neutral molecules, but negatively charged forms are particularly characteristic for oxygen as such. A second important distinction is the considerably greater mass and lower mobility of oxygen; and a third is the higher stability of bonds effected by oxygen atoms. In the general case, the single bond energy for R–O–R is about [illegible] kcal/mole, and for the hydrogen-bond R...H...R it is only 3 to 6 kcal/mole. Because of this, oxygen, in contrast to hydrogen, can also take part in chemical reactions and enter the composition of more complex molecules without cleavage of interoxygen bonds. Oxygen is present in this state in numerous saturated neutral molecules, radicals, ions of the peroxide type, and in ozonides. Finally, the number of atoms and forms of oxygen simultaneously present in a molecule is usually less than in the case of hydrogen, and therefore the kinetic complications considered in Chapter V are not so characteristic for it.

TABLE 58.

Energies of Certain Elementary Chemical Processes for Hydrogen and Oxygen in kcal/mole at 25°C

$\frac{1}{2}H_2 \to H$	– 52.09	$O + e \to O^-$	+ 72.36
$\frac{1}{2}D_2 \to D$	– 52.98	$O + 2e \to O^{2-}$	–166
$H_2 \to H_2^+ + e$	– 357.15	$1.5O_2 \to O_3$	– 34
$\frac{1}{2}H_2 + e \to H^-$	44.09	$2O_2 \to O_4$	+ 0.16
$H + e \to H^-$	+ 18.0	$\frac{1}{2}H_2 + \frac{1}{2}O_2 \to OH$	+ 10.06
$H \to H^+ + e$	315	$\frac{1}{2}H_2 + \frac{1}{2}O_2 + e \to OH^-$	+ 76.4
$\frac{1}{2}H_2 \to H^+$	– 26.3	$H_2 + \frac{1}{2}O_2 \to H_2O$	+ 57.8
$\frac{1}{2}O_2 \to O$	– 59.16	$H_2 + O_2 \to H_2O_2$	+ 31.8
$O_2 + e \to O_2^-$	+ 22*	$OH_{aq} \to H^+_{aq} + O^-_{aq}$	– 9.0**
$O_2 \to O_2^+ + e$	283.1		
$\frac{1}{2}O_2 + e \to O^-$	+ 13.20		

* According to I.A. Kazarnovsky.

** According to Hart et al.

b) Exchange of molecular oxygen by dissociation mechanisms

The dissociation energy of molecular oxygen into atoms, referred to 1 gram-atom, exceeds the dissociation energy of molecular hydrogen by only 8 kcal. Therefore, in the gas phase at high temperatures, exchange between molecules of O_2^{16} and O_2^{18}, O_2^{16} and O_2^{17}, etc., should be homomolecular, by the atomic–molecular mechanism discussed in detail for molecular hydrogen in §8, Chapter II.

$$\left.\begin{array}{l} O_2^{18} \rightleftarrows 2O^{18} \\ O_2^{16} \rightleftarrows 2O^{16} \\ O^{18} + O_2^{16} \to O^{16}O^{18} + O^{16} \\ O^{16} + O_2^{18} \to O^{16}O^{18} + O^{18} \end{array}\right\}$$

Such a reaction should proceed exponentially with an apparent activation energy

$$E_{obs} = \frac{D_{O_2}}{2} + E_{true},$$

i.e.

$$E_{obs} = 58.5 + E_{true}. \qquad (133)$$

Investigations of the photochemical and radiochemical formation of ozone from oxygen lead to the conclusion that E_{true} cannot be large, and is of the order of 4–5 kcal/mole, and therefore $E_{obs} \approx 63$ kcal/mole. The reaction should be accelerated by solid surfaces, which generate oxygen atoms into the volume of the reaction according to the scheme

$$T_{solid} + O_2 \to T_{solid}O_{ads} + O. \qquad (134)$$

The homogeneous exchange rate should obey the equation

$$w = k_{true}[O_2][O] = k_{true}[O_2]K_{diss}^{1/2}[O_2]^{1/2} = k_1[O_2]^{3/2} \qquad (135)$$

Other homogeneous mechanisms are also possible, for example, with the participation of ozone. The thermal reaction has not yet been directly studied, but the data of O'Shea and Johnston [36] on the reaction induced by the electric discharge and irradiation indicate that the semidissociative mechanism is predominant

In solutions, ionic mechanisms should predominate. This is confirmed by investigations of radiation-induced isotopic exchange between $O^{16}O^{18}$ and H_2O^{16} in aqueous solutions [180].

Without irradiation there is practically no exchange between molecular oxygen and water either directly or in presence of most solids which act as typical oxidation catalysts. Formation of hydrogen peroxide begins in neutral and aqueous media under the action of γ-radiation and ultraviolet light. At high pH, isotopic exchange according to the equation

$$O^{16}O^{18} + H_2O^{16} \to O_2^{16} + H_2O^{18}. \qquad (136)$$

is predominant.

As Fig. 53 shows, in strongly alkaline solutions the rate of isotopic exchange considerably exceeds the rate of hydrogen peroxide formation. Apart from the earliest stages, the exchange follows an exponential law, as the logarithmic plot (Fig. 54) shows. The authors showed that the initial retardation of the exchange is caused by small amounts of hydrogen peroxide, which accumulates to a constant value of 10^{-5}–10^{-6} M, and which is a powerful negative catalyst for the exchange.

At H_2O_2 concentrations below 10^{-6} M its inhibiting effect ceases and the yield per 100 ev of the absorbed γ-radiation does not change with an 8000-fold change of intensity and dose. This is also true for the photochemical reaction induced by ultraviolet light. A separate study showed that the number of initial radicals formed in γ-irradiation according to the equation

$$H_2O \xrightarrow{h\nu} HO + H. \qquad (137)$$

per 100 ev absorbed by the solution is 2.6 [181]. At pH = 9.6 the number of individual exchanges of O_2 with H_2O is greater than this, and it reaches several hundred in strongly alkaline solutions. At pH 13.9, 224 oxygen molecules are exchanged for each primary OH radical formed. Hydrogen peroxide sharply shortens the chain. A curious fact is that in alkaline solutions hydrogen peroxide exchanges its oxygen with molecular oxygen at an appreciable rate.*

To explain their findings, the authors use the results of earlier investigations of the influence of acidity on the radiochemical formation of hydrogen peroxide from $H_2 + O_2$ and $D_2 + O_2$ [182]. This led them to postulate the existence of an unusual dissociation equilibrium in solutions

$$OH \rightleftarrows O^- + H^+ \qquad (138)$$

---

*Possibly by a direct electron transfer mechanism $O_2^- + O_2 \to O_2 + \dot{O}_2^-$.

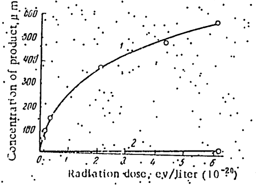


Fig. 53. Comparison of isotopic oxygen exchange (1) and hydrogen peroxide formation (2) on irradiation of alkaline solutions.

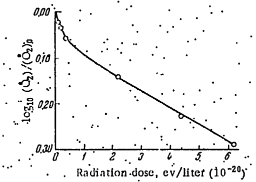


Fig. 54. Decrease of the logarithm of the relative concentration of tagged O_2 with increase of the radiation dose.

which makes probable an exchange scheme which proceeds through the agency of O^- and OH^- ions. In this scheme I represents the radiochemical equilibrium constants; K, the equilibrium constants; and k, the rate constants.

Equilibria in irradiation:

$$\left.\begin{array}{lll} \text{a)} & H_2O \rightleftarrows H + OH & I_1 \\ \text{b)} & H_2O \rightleftarrows \frac{1}{2} H_2 + \frac{1}{2} H_2O_2 & I_2 \\ \text{c)} & H + \dot{O}_2 \rightleftarrows H\dot{O}_2 & I_3 \end{array}\right\} \qquad (139)$$

Ionization equilibria in primary solution:

$$\left.\begin{array}{lll} \text{a)} & OH \rightleftarrows O^- + H^+ & K_1 \\ \text{b)} & H\dot{O}_2 \rightleftarrows H^+ + \dot{O}_2^- & K_2 \\ \text{c)} & H_2O \rightleftarrows H^+ + HO^- & K_3 \end{array}\right\} \qquad (140)$$

Nonequilibrium stages:

$$\left.\begin{array}{lll} \text{a)} & O^- + \dot{O}_2 \rightarrow \dot{O}^- + O_2 & k_1 \\ \text{b)} & \dot{O}^- + OH^- \rightarrow O^- + \dot{O}H^- & k_2 \\ \text{c)} & O^- + H_2O_2 \rightarrow H_2O + O_2^- & k_3 \\ \text{d)} & \dot{O} + H_2O_2 \rightarrow H_2\dot{O} + O_2^- & k_4 \\ \text{e)} & O_2^- + O_2^- \rightarrow O_2^{2-} + O_2 & k_5 \end{array}\right\} \qquad (141)$$

In strongly alkaline solutions, the authors assume complete dissociation of OH into O^- and H^+ ions.

The main exchange of tagged oxygen is effected by alternation of the reactions (141, a and b). Principal chain termination is effected by reactions (141, c, d and e). On this basis the authors derive the following equations for the exchange kinetics and the radiation yield:

$$\frac{d[O_2]}{dt} = \frac{I_1}{k_3[H_2O_2]\left[\frac{1}{k_1[\dot{O}_2]} + \frac{1}{k_2[OH^-]}\right]}; \qquad (142)$$

$$\gamma_{100\,ev} = \frac{1}{k_3[H_2O_2]\left[\frac{1}{k_1} + \frac{[\dot{O}_2]}{k_2[OH^-]}\right]}, \qquad (143)$$

which satisfactorily represent the characteristics of the process.

It is significant that O_2^- ions, which play such an important part in the reactions of oxygen in solutions, do not induce chain exchange, although non-chain exchange

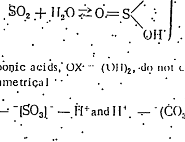
$$O_2^- + \dot{O}_2 \rightarrow \dot{O}_2^- + O_2 \qquad (144)$$

cannot be excluded.

The above examples demonstrate the wide occurrence and peculiar character of dissociative atomic and ionic mechanisms of the isotopic exchange of oxygen.

c) Exchange of oxygen in water and anions

Urey and others [183, 184] in connection with the problem of obtaining oxygen enriched with O^{18}, made a detailed study of the isotopic exchange of oxygen in carbon dioxide and sulfur dioxide with aqueous solutions of the corresponding acids and salts. When the acid anhydrides are dissolved in water, the corresponding ortho-forms are obtained, in dynamic equilibrium with the oxides

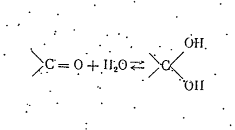


(145)

The formulas of sulfurous and carbonic acids, $OX=(OH)_2$, do not convey quite accurately the true structure of the anions, which are completely symmetrical

$$H^+ - {}^-[SO_3]^- - H^+ \text{ and } H^+ - {}^-(CO_3)^- - H^+$$

Therefore, by repeated formation and decomposition of the acids, oxygen isotope equilibrium will be rapidly established in solution, and CO_2 and SO_2 blown through the water will leave with O^{17} and O^{18} contents corresponding to equipartition. Some authors assume a more far-reaching reversible hydration with formation of orthosulfurous and orthocarbonic acids

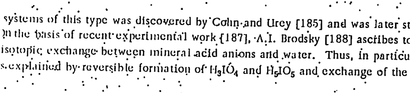


(145a).

The reversible reaction

(146)

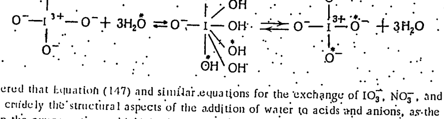
is usually held to play the decisive role in the isotopic exchange of organic carbonyl compounds with water



$$RCHO + H_2\overset{*}{O} \rightleftarrows RCH\begin{matrix} OH \\ \overset{*}{O}H \end{matrix} \rightleftarrows RCH\overset{*}{O} + H_2O. \qquad (146a)$$

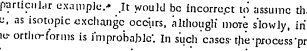
Rapid oxygen exchange in systems of this type was discovered by Cohn and Urey [185] and was later studied by numerous workers [186]. On the basis of recent experimental work [187], A.I. Brodsky [188] ascribes to the ortho-forms the decisive role in isotopic exchange between mineral acid anions and water. Thus, in particular, the exchange of HIO_3 with $H_2\overset{*}{O}$ is explained by reversible formation of H_3IO_4 and H_5IO_5 and exchange of the IO_4^- ion with $H_2\overset{*}{O}$

(147)



(147a)

It must be remembered that Equation (147) and similar equations for the exchange of IO_3^-, NO_3^-, and HSO_4^- ions represent only very crudely the structural aspects of the addition of water to acids and anions, as the structural distinctions between the oxygen atoms which, in the scheme, are joined to the central atom of the anion (or acid) by one and two bonds respectively are illusory. This is conveyed somewhat better by the scheme



(148)

of which Equation (147a) is a particular example.* It would be incorrect to assume that ortho-forms play a universal role in oxygen exchange, as isotopic exchange occurs, although more slowly, in salt and weakly alkaline solutions, when existence of the ortho-forms is improbable. In such cases the process probably occurs according to the scheme

$$CO_3^{2-} + C\overset{*}{O}_2 \rightarrow [CO_3^{2-} \cdot \overset{*}{O}_2C] \rightarrow CO_2 + C\overset{*}{O}_3^{2-} \qquad (149)$$

and reduces to migration of an oxygen atom and two electrons in the intermediate complex. Oxygen transfer by a purely electronic mechanism is also possible in solutions. For example, as experiments with chlorine dioxide with tagged chlorine show [189], the latter exchanges rapidly with ClO_2^- ions according to the scheme

$$\overset{*}{Cl}O_2 + ClO_2^- \longrightarrow \overset{*}{Cl}O_2^- + ClO_2 \qquad (150)$$

It is evident that if the oxygen in ClO_2 is tagged, even by means of O^{18}, oxygen exchange by a purely electronic mechanism can easily be effected. Therefore it would be incorrect to assume that the formation of ortho-forms by anions, postulated by A.I. Brodsky to explain rapid exchange of CO_2 in solutions, is the only or the fundamental mechanism of oxygen exchange in the liquid phase, although this mechanism is probably very common.

Of the other mechanisms suggested for the isotopic exchange of oxygen in water, we will refer again to the reversible dissociation into the acid anhydride and water, shown above for CO_2 and SO_2. Haissinsky and Daudel [190] consider this mechanism to be very common even among stable acids with nonvolatile anhydrides, and in particular in the exchange of CrO_4^{2-} ions with $H_2\overset{*}{O}$ in acid solutions

$$\begin{aligned} H_2CrO_4 &\rightleftarrows CrO_3 + H_2O, \\ CrO_3 + H_2\overset{*}{O} &\rightleftarrows H_2CrO_3\overset{*}{O}. \end{aligned} \qquad (151)$$

This is a complete, but unlikely, analog of the mechanism of CO_2 and SO_2 exchange. Other mechanisms by way of reversible hydrolysis have been postulated, for example

$$\begin{aligned} 2CrO_4^{2-} + H_2\overset{*}{O} &\rightleftarrows Cr_2O_7^{2-} + \overset{*}{O}H^- + OH^- \rightleftarrows \\ &\rightleftarrows CrO_4^{2-} + CrO_3\overset{*}{O}^{2-} + H_2O, \end{aligned} \qquad (151a)$$

addition and removal of hydroxyl ions, etc. [191]. The applicability of such mechanisms is very limited.

§21. Isotopic Exchange of Halogens

In the case of the halogens, only artificial radioactive isotopes are of practical importance as tagged atoms at present. For iodine, these are primarily I^{131} with $\tau_{1/2}$ = 8 days, and I^{126} with $\tau_{1/2}$ 13.1 days. Even now the short-lived I^{128} with $\tau_{1/2}$ = 30 minutes, very easily obtained by neutron bombardment of ordinary iodine, is sometimes used in research work. The bromine isotope most often used is Br^{82} with $\tau_{1/2}$ 34 hours, which usually contains the radioisomers Br^{80} with $\tau_{1/2} \approx$ 4.5 hours and 18 minutes. The use of Br^{77} with $\tau_{1/2}$ 57.4 hours is promising. The chlorine isotopes used are Cl^{36} with $\tau_{1/2} \approx 0.44 \cdot 10^6$ years and Cl^{38} with $\tau_{1/2}$ = 38.5 minutes. The only isotope which can be considered as tagged fluorine is F^{18} with $\tau_{1/2} \approx$ 107 minutes. All the isotopes of Mendeleev's eka-iodine (astatine) are short-lived, and at present are of no value for kinetic studies.

The radioactive isotopes of chlorine are inconvenient because of their half-lives which fall outside the optimum range,* and therefore, in future, work with individual stable isotopes of chlorine is likely to become usual. Their separation and determination do not present special difficulties at the present level of isotope techniques. Subsequently the use of stable bromine isotopes may also prove practicable.

Investigations of the isotopic exchange of halogens began immediately after the discovery of artificial radioactivity in connection with the search for suitable starting materials for the preparation of radioactive isotopes by the Szilard–Chalmers method [192].

Before the discovery of uranium fission, the principal sources of radioactive halogens were nuclear reactions of neutron capture

$$\left.\begin{aligned} I^{127} + n_0^1 &\rightarrow \overset{*}{I}^{128} + h\nu, \\ Br^{81} + n_0^1 &\rightarrow \overset{*}{Br}^{82} + h\nu, \\ Cl^{37} + n_0^1 &\rightarrow \overset{*}{Cl}^{38} + h\nu, \text{ etc.} \end{aligned}\right\} \qquad (152)$$

discovered by Fermi and his associates [193]. The neutron binding energy in the nucleus is very high, of the order of 7,000,000 ev. Most of this energy is emitted in the form of hard γ-radiation quanta, which confer recoil energies of 100 ev and over to the nuclei of the radioactive halogens formed.

Szilard and Chalmers were the first to show the possibility of using the increased chemical activity of the recoil atoms of the (n, γ) reaction for the production of enriched preparations of artificial radioactive isotopes.

---

*Incidentally, we may note that the intermediate form $H_6IO_7^-$, with coordination number 7, assumed by A.I. Brodsky and N.A. Vysotskaya [108], is doubtful.

*Very arbitrarily, the most convenient range of half-life periods for chemical work is the range covering 6 orders of magnitude from 24 hours to 10,000 years.

Subsequently this method became widely used, and even now remains of preparative importance.

The parent substances used in the Szilard-Chalmers method are compounds of the appropriate element which do not readily enter into isotopic exchange under irradiation conditions. Conversely, it is desirable, for furtherance, to convert the resultant radioactive isotope, without dilution by stable isotopes, into some easily exchanging compound. Naturally, the development of this method made necessary extensive qualitative investigation of the exchange capacities of various types of compounds for different elements. Many of these investigations concerned the halogens. These revealed certain general relationships between ease of exchange and chemical structure of the exchanging compounds. Thus, it was found that halogens contained in organic molecules and covalently linked to carbon do not readily exchange with the radioactive isotopes formed which are initially in the form of individual ions or free atoms. The anions of oxy-acids containing quinque- or septivalent halogens in the central atom, behave similarly. This has been shown for ClO_3^-, ClO_4^-, BrO_3^-, IO_4^- in solutions [193], solids, and in melts [194, 195]. The behavior of free halogens in the form of the elements or simple negative ions is quite different. No formation of radioactive halogens in separable form is observed on neutron bombardment of aqueous solutions of MeHal salts, halogen vapors, or crystalline halides.

Subsequent investigations showed that the true picture in the bombardment of organic halides is much more complex. In particular, at the instant of formation, "hot atoms," which are free atomic ions rich in energy, react chemically even with difficultly exchanging molecules of the parent substances, which may be present in any state of aggregation [196]. According to the experimental conditions, from 30 to 70% of the radioactive halogen formed is retained by the parent substance. Despite complicating circumstances, experiments on the isolation of radioactive products of (n, γ) processes have yielded interesting data on the exchange capacity of halogens.

The first systematic studies of thermal isotopic exchange in solutions and between solid halides and vapors were carried out here in connection with an investigation of the role of atom transfer in catalysis. In this connection it was necessary to determine whether any parallelism exists between the catalytic action of metal halides in halogenation and in certain other types of reactions, and their reactivities in isotopic exchange [195, 197]. The most inert of the metal halides in the solid state were found to be the alkali metal halides (NaBr, KBr, NaI, KI). Below 200°C at low specific radioactivities no appreciable isotopic exchange could be detected between these halides and either free halogen vapors (Br_2, I_2) or hydrogen halides (HBr, HI). The behavior of calcium chloride is analogous. With increased sensitivity of the methods and a large increase in the degree of dispersion of the layers some exchange could be detected even in these salts. Determinations of the mobilities of halide ions in the lattices of alkali and alkaline earth halides based on transference numbers and self-diffusion of tagged halides indicate the difficulty of displacement of halide layers in these layers. Such determinations carried out by A. Murin and Yu. Taush [198] with silver bromide, with $\overset{*}{Br}{}^{82}$ as tracer, showed that even at 300°C the diffusion coefficient D of the bromide ion is only $3 \cdot 10^{-11}$ cm^2/second. This is thousands of times smaller than D for silver ions, determined under the same conditions with the use of $\overset{*}{Ag}{}^{110}$. This and other observations make it very probable that the observed absence of exchange of bromine and HBr with many halides of uni- and bivalent metals in the solid state is due to lack of appreciable mobility of Hal^- and Hal_2 in these crystals at the experimental temperatures. This explanation is in agreement with the results of subsequent investigations by A.Ya. Fialkov and Yu.P. Nazarenko [199]. At the same temperature slight exchange in the crystalline state and in organic solvents with low dielectric constants κ is found to occur in $ZnBr_2$, $CdBr_2$, $MnBr_2$, $HgBr_2$. Magnesium bromide occupies an intermediate position between $CaBr_2$ and $ZnBr_2$. Very rapid exchange was found, both in the solid state and in organic solvents with low κ, for $AlBr_3$, AlI_3, $FeBr_3$, $CrBr_3$, which are good complex formers and typical acid catalysts of the nonprotonic type. In liquids with high values of κ, which induce electrolytic dissociation of the dissolved halides, the latter exchange very rapidly and completely both with free halides and with each other. This was observed by Szilard and Chalmers [192] for I_2 with potassium iodide; by ourselves [198, 200] for many bromides with bromine and iodides with iodine, by Olson et al. [200] for Cl_2 with chlorides. In many cases the exchange probably proceeds according to the equation

$$\mathrm{Hal\overset{*}{Hal}} + \mathrm{Hal}^- \rightarrow [\mathrm{Hal_2\overset{*}{Hal}}]^- \rightarrow \mathrm{Hal_2} + \overset{*}{\mathrm{Hal}}{}^- \qquad (153)$$

involving Hal^- formed by electrolytic dissociation. On the other hand, exchange between Hal^- and Hal of oxy-acid occurs with very great difficulty in $\overset{*}{Br}$ + BrO_3^-, $\overset{*}{Cl}{}^-$ + ClO_3^- and $\overset{*}{Cl}{}^-$ + ClO_4^-. This was first shown for aqueous solutions by Fermi et al. [193]. Later we showed that, even in melts, exchange of MeBr with $MeBrO_3$, MeI with $MeIO_3$, and MeCl with $MeClO_4$ [195, 196] at T of the order of 500°C is far from complete after tens of minutes.

K.B. Zaborenko, M.B. Neiman and V.I. Samsonov [201] were able to measure exchange between KI and KIO_3 after prolonged heating above 200°C in sealed tubes under increased pressure.

The connection between the structure of ordinary and complex halogen compounds and their exchange capacity was studied by A.S. Polesitsky [202] and A.A. Grinberg et al. [203]. An extensive investigation of the exchange capacity of inorganic halides was made by Ya.A. Fialkov and Yu.P. Nazarenko [204]. The exchange of bromine was studied in compounds of 28 elements separately.

Having obtained results similar to ours for aqueous solutions of KBr, $ZnBr_2$, $CdBr_2$, $HgBr_2$ and others, these authors showed that very rapid exchange of radioactive bromine occurs with bromine in the solvent in the cases of aluminum bromide, boron bromide, thallium tribromide, phosphorus tribromide, and stannic tetrabromide, dissolved in bromine. The bromides of phosphorus, arsenic, and antimony, dissolved in carbon tetrachloride, also exchange rapidly with bromine: $ZnBr_2$, $CdBr_2$, $HgBr_2$, $AlBr_3$, $SbBr_3$ and $BiBr_3$ exchange rapidly, and PBr_3, $AsBr_3$, $SiBr_4$ and $SnBr_4$ slowly, with bromide ions. A comparison of the exchange capacities of similar compounds of elements of the same subgroup of the periodic system is interesting. The exchange rate of P, As, and Sb bromides increases steadily with atomic weight. In the fourth group the situation is more complex: in particular, carbon tetrabromide occupies an intermediate position between $SiBr_4$ and $SnBr_4$ in its case of exchange with $\mathrm{Br\overset{*}{Br}}$ and $\mathrm{AlBr_2\overset{*}{Br}}$.

Valuable material supplementing the data on bromides is found in the later publications by the same authors on the isotopic exchange of iodine [205], which are closely connected with the earlier publications by Ya.A. Fialkov and his school [206-208] on complex compounds of aluminum halides and polyhalides [211]. An investigation of the exchange of iodides of metals from different groups of the periodic system showed that all iodides which are easily soluble in molten iodine – KI, Cu_2I_2, AgI, CaI_2, AlI_3, SnI_4, AsI_3, SbI_3 – exchange their iodine completely or almost completely on heating in sealed tubes for 1 hour. These experiments were generally performed at 150°C. In these conditions incomplete exchange was found only for ZnI_2 and CdI_2, which are not easily soluble in liquid iodine. Incomplete exchange is more common between iodine vapor and iodide crystals. For example, KI exchanges only partially in 4 hours at 250°C, and ZnI_2 and CdI_2 practically do not exchange at all at 250°. The same systems exchange completely in ethanol and ethyl acetate solutions at a considerably lower temperature (77-78°C). Curious results were obtained in investigations of the exchange of KI with iodides of certain metals at high temperatures (250-450°), close to their boiling points. In such conditions the solid salt is in contact both with the strongly heated melt and with the vapor of the second component, but nevertheless arsenious iodide and stannic iodide almost do not exchange with $K\overset{*}{I}$, while ZnI_2, HgI_2, AlI_3, and SbI_3 exchange with KI completely.

All the investigations cited are characterized by a lack of extensive quantitative kinetic data and detailed analysis of phase conditions; therefore the findings are not of a strict character and it is probable that considerable corrections would result from comparisons of the exchange capacities in other, more comparable conditions. However, despite these evident defects, a qualitative comparison of the results for numerous substances reveals the existence of several exchange mechanisms. An example is the association mechanism, which is possible both for Hal_2 and for Hal^- ions. A halide MeHal, without breaking its bond with the molecule (crystal lattice), or splitting off in the form of a Hal^- ion, forms an addition complex with Hal_2, on the formation of which the polyhalides, well known in inorganic chemistry, are based. If such polyhalides are sufficiently labile, rapid exchange by way of their reversible formation and decomposition is possible, according to the equations

$$\left.\begin{aligned} &1)\ \mathrm{MeHal}_n + \mathrm{\overset{*}{Hal}Hal} \leftrightarrows \mathrm{MeHal}_{n+1}\,\overset{*}{\mathrm{Hal}} \rightleftarrows \mathrm{MeHal}_{n-1}\,\overset{*}{\mathrm{Hal}} + \mathrm{Hal}_2,\\ &\text{or}\\ &2)\ a)\ \mathrm{MeHal}_n \rightleftarrows \mathrm{MeHal}^+_{n-1} + \mathrm{Hal}^-;\\ &\quad\ b)\ \mathrm{Hal}^- + \mathrm{Hal\overset{*}{Hal}} \rightleftarrows (\mathrm{HalHal\overset{*}{Hal}})^- \rightleftarrows \mathrm{Hal}_2 + \overset{*}{\mathrm{Hal}}{}^-;\\ &\quad\ c)\ \overset{*}{\mathrm{Hal}}{}^- + \mathrm{MeHal}^+_{n-1} \rightleftarrows \mathrm{MeHal}_{n-1}\,\overset{*}{\mathrm{Hal}}. \end{aligned}\right\} \qquad (154)$$

If the complexes are very stable, this exchange mechanism may become ineffective. In particular, there are reports of the decreased exchange capacity of bromine in mercuric bromide and antimony tribromide on formation of the complex anions $HgBr_4^{2-}$ and $SbBr_4^-$. In solvents with high dielectric constants and in melts, a dissociation mechanism is common, by way of dissociation into Hal^- ions and recombination of the ions. In many cases rapid exchange takes place through dissociation of halogen molecules into atoms with subsequent formation of labile addition complexes. This mechanism has been proved for some cases both of photochemical and of thermal exchange.

Exchange with alternate reduction and oxidation has also been postulated for halides of elements with variable valences. According to our data, this mechanism is possible for the exchange of $CuBr_2$ with Br_2

$$\left.\begin{array}{l} 2CuBr_2 \rightarrow Cu_2Br_2 + Br_2; \\ \overset{*}{Br}_2 + Cu_2Br_2 \rightarrow 2CuBr\overset{*}{Br}. \end{array}\right\} \qquad (155)$$

In the case of PCl_3, Fialkov and Nazarenko, together with Haissinsky and Daudel [190] consider that the high temperature exchange with Cl_2 probably occurs according to the scheme

$$\left.\begin{array}{l} PCl_5 \rightleftarrows PCl_3 + Cl_2; \\ PCl_3 + Cl\overset{*}{Cl} \leftrightarrows PCl_4\overset{*}{Cl}. \end{array}\right\} \qquad (156)$$

The small amount of exchange between SnI_4 and KI at 390°C is ascribed by these authors to iodine formed by reversible dissociation

$$\left.\begin{array}{l} SnI_4 \rightleftarrows SnI_2 + I_2; \\ I_2 + K\overset{*}{I} \rightleftarrows KI + I\overset{*}{I}; \\ SnI_2 + I\overset{*}{I} \rightleftarrows SnI_3\overset{*}{I} \end{array}\right\} \qquad (157)$$

The free iodine acts as a peculiar catalyst – carrier, which carries atoms of radioactive iodine from $K\overset{*}{I}$ to SnI_4. There are also more special mechanisms, such as halogen exchange in aqueous solutions with intermediate formation of $HalO^-$ and $HalO_2^-$ ions.

The existence of a wide gradation of exchange rates for different halides creates highly favorable conditions for catalytic transfer, which has already been mentioned. Because of their ability to exchange their halogen readily with halogens of various other compounds, $AlHal_3$, $FeHal_3$, $CeHal_3$ etc., present even in very low concentrations, can exert a very strong catalytic action on the exchange of substances which do not readily exchange with each other directly. Because of the easy photochemical dissociation of halogens into atoms, the isotopic exchange of inorganic halides can be easily accelerated photocatalytically by exposure to light.

§22. Mechanism and Kinetics of the Exchange of Organic Halides

The isotopic exchange of organic halides with free halogens, halide ions, and inorganic halides has been studied more than any other group of isotopic exchange reactions. The exchange mechanisms are also better substantiated, as this is the only group for which systematic quantitative determinations of the kinetic constants are available. The qualitative aspects of the exchange had been established in general form even before the war [196] on the basis of the data given in Table 59.

These data are largely taken from the results of investigations made in 1935-1937 in our laboratory in the Leningrad Institute of Chemical Physics. In these investigations, so far as solubility allowed, exchange was studied in concentrated liquid mixtures of the exchanging substances. If a metal bromide had low solubility, its crystals were shaken for a suitable time with the liquid organic bromide. In much rarer instances both the exchanging bromides were dissolved in a common solvent. The high concentrations made the conditions highly favorable for exchange, and negative results indicate very low rate constants; conversely, complete exchange may conceal processes with fairly large rate differences, and a considerable proportion of these exchange reactions, when carried out in solvents of similar physicochemical properties but not containing bromine, occurs at measurable rates. This must be taken into account in studying the deductions based on this table and Table 60 (see below), taken from our 1938 review [194].

"Isotopic exchange of bromine does not occur at all between molecules of various organic bromides over the whole temperature range from 0° to the boiling point of the particular mixture. It is quite evident that here we are dealing with processes which require many* tens of thousands of cals/mole. Exchange between halogen

---

*It would be more accurate to say "several."

TABLE 59

Qualitative Characteristics of Isotopic Exchange of Organic Halides [194].

Serial No.	Reaction	State	Temperature	Exchange characteristics	Notes	Literature
	Exchange of Br_2					
1	C_2H_5Br	Liquid	Room	No exchange	Bromine vapor blown through liquid	N. E. Brezhneva and S. Z. Roginsky [194]
2	$C_2H_4Br_2$	"	"	"		
3	$C_5H_{11}Br$	"	"	"		
4	C_6H_5Br	"	"	"		
5	α-$C_{10}H_7Br$	"	"	"		
6	$C_3H_6Br_2$	"	"	"		
7	$Br^- + C_2H_5Br$	"	"	"		Roginsky and Gopshtein [45]
8	$I^- + C_2H_5I$	"	"	"		Szilard and Chalmers [199]
	Exchange of I_2					
9	C_2H_5I	Solution in alcohol	On heating	"		Hull, Shiflet and Lind [209]
10	C_2H_5I	I_2 in C_6H_5I solution	"	"		
11	CHI_3	"	"	"		
12	CHI_3	Solution in alcohol	"	Partial		
	Exchange of HBr					
13	C_6H_5Br	Liquid	Room	No exchange	HBr vapor blown through liquid	N. E. Brezhneva and S. Z. Roginsky [194]
14	α-$C_{10}H_7Br$	"	"	"		
15	β-$C_{10}H_7Br$	Melt	60°	"		
	Exchange of $AlBr_3$					
16	C_2H_5Br	Liquid	−21 −38°	Complete	$AlBr_3$ dissolved in liquids	
	C_2H_5Br	"	−30°	Partial		
17	$C_2H_4Br_2$	"	0-100°	Complete		
18	$C_5H_{11}Br$	"	0-100°	Incomplete	" "	
19	C_3H_6Br	"	Room	Complete		
20	$CHBr_3$	"	"	"		N. E. Brezhneva and S. Z. Roginsky [194]
21	CH_3Br	"	"	"		
22	C_6H_5Br	"	20-120°	Partial		
23	p-$C_6H_4Br_2$	Solution in benzene	20-80°	"		
24	α-$C_{10}H_7Br$	Liquid	20-160°	Almost none		
25	β-$C_{10}H_7Br$	Melt	60°	"		
26	$C_6H_3Br_3$	Solution in benzene	20-80°	Partial		
27	$C_6H_5CH_2Br$	Liquid	Room	Complete		

exchange takes place through dissociation of halogen molecules into atoms with subsequent formation of labile addition complexes. This mechanism has been proved for some cases both of photochemical and of thermal exchange.

Exchange with alternate reduction and oxidation has also been postulated for halides of elements with variable valencies. According to our data, this mechanism is possible for the exchange of $CuBr_2$ with Br_2.

$$\left.\begin{array}{l} 2CuBr_2 \rightleftarrows Cu_2Br_2 + Br_2; \\ \overset{*}{Br}_2 + Cu_2Br_2 \rightarrow 2CuBr\overset{*}{Br}. \end{array}\right\} \qquad (155)$$

In the case of PCl_3, Fialkov and Nazarenko, together with Haissinsky and Daudel [190] consider that the high temperature exchange with Cl_2 probably occurs according to the scheme

$$\left.\begin{array}{l} PCl_5 \rightleftarrows PCl_3 + Cl_2; \\ PCl_3 + Cl\overset{*}{Cl} \rightleftarrows PCl_4\overset{*}{Cl}. \end{array}\right\} \qquad (156)$$

The small amount of exchange between SnI_4 and KI at 390°C is ascribed by these authors to iodine formed by reversible dissociation

$$\left.\begin{array}{l} SnI_4 \rightleftarrows SnI_2 + I_2; \\ I_2 + K\overset{*}{I} \rightleftarrows KI + I\overset{*}{I}; \\ SnI_2 + I\overset{*}{I} \rightleftarrows SnI_3\overset{*}{I}. \end{array}\right\} \qquad (157)$$

The free iodine acts as a peculiar catalyst – carrier, which carries atoms of radioactive iodine from $K\overset{*}{I}$ to SnI_4. There are also more special mechanisms, such as halogen exchange in aqueous solutions with intermediate formation of $HalO^-$ and $HalO_2^-$ ions.

The existence of a wide gradation of exchange rates for different halides creates highly favorable conditions for catalytic transfer, which has already been mentioned. Because of their ability to exchange their halogen readily with halogens of various other compounds, $AlHal_3$, $FeHal_3$, $CeHal_3$ etc., present even in very low concentrations, can exert a very strong catalytic action on the exchange of substances which do not readily exchange with each other directly. Because of the easy photochemical dissociation of halogens into atoms, the isotopic exchange of inorganic halides can be easily accelerated photocatalytically by exposure to light.

§ 22. Mechanism and Kinetics of the Exchange of Organic Halides

The isotopic exchange of organic halides with free halogens, halide ions, and inorganic halides has been studied more than any other group of isotopic exchange reactions. The exchange mechanisms are also better substantiated, as this is the only group for which systematic quantitative determinations of the kinetic constants are available. The qualitative aspects of the exchange had been established in general form even before the war [196] on the basis of the data given in Table 59.

These data are largely taken from the results of investigations made in 1935–1937 in our laboratory in the Leningrad Institute of Chemical Physics. In these investigations, so far as solubility allowed, exchange was studied in concentrated liquid mixtures of the exchanging substances. If a metal bromide had low solubility, its crystals were shaken for a suitable time with the liquid organic bromide. In much rarer instances both the exchanging bromides were dissolved in a common solvent. The high concentrations made the conditions highly favorable for exchange, and negative results indicate very low rate constants; conversely, complete exchange may conceal processes with fairly large rate differences, and a considerable proportion of these exchange reactions, when carried out in solvents of similar physicochemical properties but not containing bromine, occurs at measurable rates. This must be taken into account in studying the deductions based on this table and Table 60 (see below), taken from our 1938 review [194].

" Isotopic exchange of bromine does not occur at all between molecules of various organic bromides over the whole temperature range from 0° to the boiling point of the particular mixture. It is quite evident that here we are dealing with processes which require many* tens of thousands of cals/mole. Exchange between halogen

---

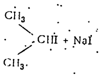
*It would be more accurate to say "several."

TABLE 59

Qualitative Characteristics of Isotopic Exchange of Organic Halides [194].

Serial No.	Reaction	State	Temperature	Exchange characteristics	Notes	Literature
	Exchange of Br_2					
1	C_2H_5Br	Liquid	Room	No exchange	Bromine vapor blown through liquid	N.E. Brezhneva and S.Z. Roginsky [194]
2	$C_2H_4Br_2$	"	"	"		
3	$C_5H_{11}Br$	"	"	"		
4	C_6H_5Br	"	"	"		
5	α-$C_{10}H_7Br$	"	"	"		
6	$C_3H_6Br_2$	"	"	"		
7	$Br^- + C_2H_5Br$	"	"	"		Roginsky and Gopshtein [45]
8	$I^- + C_2H_5I$	"	"	"		Szilard and Chalmers [192]
	Exchange of I_2					
9	C_2H_5I	Solution in alcohol	On heating	"		Hull, Shiflet and Lind [209]
10	C_2H_5I	I_2 in C_6H_5I solution	"	"		
11	CHI_3	"	"	"		
12	CHI_3	Solution in alcohol	"	Partial		
	Exchange of HBr					
13	C_6H_5Br	Liquid	Room	No exchange	HBr vapor blown through liquid	N.L. Brezhneva and S.Z. Roginsky [194]
14	α-$C_{10}H_7Br$	"	"	"		
15	β-$C_{10}H_7Br$	Melt	60°	"		
	Exchange of $AlBr_3$					
16	C_2H_5Br	Liquid	−21 – 38°	Complete	$AlBr_3$ dissolved in liquids	
	C_2H_5Br	"	−30°	Partial		
17	$C_2H_4Br_2$	"	0-100°	Complete		
18	$C_5H_{11}Br$	"	0-100°	Incomplete	" "	
19	C_3H_6Br	"	Room	Complete		
20	$CHBr_3$	"	"	"		N.L. Brezhneva and S.Z. Roginsky [194]
21	CH_3Br	"	"	"		
22	C_6H_5Br	"	20-120°	Partial		
23	p-$C_6H_4Br_2$	Solution in benzene	20-80°	"		
24	α-$C_{10}H_7Br$	Liquid	20-160°	Almost none		
25	β-$C_{10}H_7Br$	Melt	60°	"		
26	$C_6H_3Br_3$	Solution in benzene	20-80°	Partial		
27	$C_6H_5CH_2Br$	Liquid	Room	Complete		

TABLE 59 (continued)

Serial No.	Reaction	State	Temperature	Exchange characteristics	Notes	Literature
28	CBr_4	Liquid	Room	Complete		N.E. Brezhneva and S.Z. Roginsky [194]
29	$AlI_3 + C_2H_5I$	"	"	"	AlI_3 and $AlCl_3$ dissolved in liquid	
30	$AlCl_3 + C_2H_4Cl_2$	"	"	Appreciable		
31	$FeBr_2 + C_2H_5Br$	"	"	"		
32	$FeBr_2 + C_6H_5Br$	"	"	"		
33	$Fe_3Br_8 + C_6H_5Br$	"	"	Good		N.E. Brezhneva and S.Z. Roginsky [194]
34	$MgBr_2 + C_6H_5Br$	"	"	No exchange		
35	$MgBr_2 + C_2H_5Br$	"	"	"	Bromide crystals put for some time into RBr	
36	$CdBr_2 + C_2H_5Br$	"	"	"		
37	$CdBr_2 + C_6H_5Br$	"	"	"		
38	$ZnBr_2 + C_2H_5Br$	"	20-38°	"		
39	$ZnBr_2 + C_6H_5Br$	"	20-80°	"		
40	$ZnBr_2 + \alpha\text{-}C_{10}H_7Br$	"	20-100°	"		
41	$ZnBr_2 + C_2H_5Br$	"	Room	"		
42	$MnBr_2 + C_6H_5Br$	"	Up to 80°	"		
43	$MnBr_2 + \alpha\text{-}C_{10}H_7Br$	"	"	"		
44	$HBr + C_2H_5Br$	"	Room	"		N.E. Brezhneva and S.Z. Roginsky [194]
45	$CeBr_3 + C_2H_5Br$	"	"	Partial		
46	$CaBr_2 + C_2H_5Br$	"	"	No exchange	Ditto	
47	$CaBr_2 + C_2H_5Br$	"	"	"		
48	$CaBr_2 + C_5H_{11}Br$	"	"	"		
49	$C_2H_5Br + C_2H_4Br_2$	"	"	"	Liquids mixed	N.E. Brezhneva and S.Z. Roginsky [194]
50	$C_2H_5Br + C_5H_{11}Br$	"	Up to 38°	"		
51	$C_2H_5Br + C_6H_5Br$	"	"	"		
52	$CH_3I + NaI$	Aqueous alcohol solution	Room	Partial		
53	$CH_2CHCH_2I + NaI$	"	"	Almost none		Juliusburger; Topley and Weiss [210]
54	$CH_3CH_2I + NaI$	"	"	"		
55	$CHI_3 + NaI$	Solution in acetone	"	"		
56	$NaI + I_2$	Aqueous alcohol solution	"	Considerable		
57	 $(CH_3)_2CHI + NaI$	"	"	Almost none		

molecules (Cl_2, Br_2, I_2) and the corresponding halogen derivatives is also extremely slow in absence of actinic light. This also applies to hydrogen bromide.

The sole exception is the system $CH_3Br + HBr$, in which the exchange is rapid. Possibly this is the result of the anomalous behavior of the first term of a homologous series, common in organic chemistry.

On the other hand, exchange with $AlBr_3$, which can form complexes analogous to inorganic polybromides, proceeds relatively easily, and some simple laws can be readily detected; for example, the exchange of aliphatic bromides and iodides is in general considerably more rapid than the exchange of aromatic bromides and iodides.

The exchange rate in the aliphatic series decreases with increasing complexity of the radical. Equipartition is always found in the cases of ethyl and methyl bromides in which aluminum bromide is dissolved even if only 1-2 minutes have elapsed from the time of solution to hydrolysis and the temperature of the bromide is considerably below zero.

On the other hand, aromatic bromides exchange their bromine with aluminum bromide at finite although fairly considerable rates, and several hours are required at room temperature to reach equipartition.

The situation is quite analogous for aliphatic dibromides and tribromides, and, as special experiments show (Table 60), all the halogen atoms of the given compound are exchanged. Table 60 contains data on the exchange of certain organic bromides with aluminum bromide, and the activities α are compared with the theoretically calculated values for the exchange of one and all the atoms. The results of this comparison are quite conclusive.

Exchange in aromatic halogen derivatives with halogen atoms in the nucleus is considerably slower. No exchange can be detected at room temperature, and temperatures of 80-100° are necessary to detect its occurrence in a measurable time; this has been shown for mono- and dibromobenzene and for isomeric naphthalene monobromides. At higher temperatures the exchange becomes appreciable, but side reactions of polymerization and resinification, catalyzed by aluminum bromide, appear. This sharp difference between the properties of aliphatic and aromatic bromides is not unexpected, since the great difference in the mobility of bromine in these two states has long been known in organic chemistry. The validity of the conclusions drawn is confirmed by experiments on the exchange of benzyl bromide. In this case the bromine is in the side chain, and the exchange is found to be complete at room temperature.

It is interesting to compare these results with literature data on the exchange of alkyl halides with halide ions in solutions. This was studied by Hull, Shiflet, and Lind [209] for the system $CH_3I - KI$ in ether, and by Juliusberger, Topley and Weiss [210] for other iodides.

In the sole case of $CH_3I + I^-$ there has been an approximate evaluation of the heat of activation (~16.5 kcal), which is in good agreement with theoretical estimates.

We are concerned with the relationship between ease of exchange and structure. Only $CH_2 = CHCH_2I$ and CH_3I exchange easily, while the others do so very slowly. The anomalous behavior of CH_3Br has already been noted above with regard to the exchange between methyl bromide and hydrogen bromide. In the case of $CH_2 = CHCH_2I$, the double bond probably exerts an activating effect on the adjacent halogen. This may be correlated with the rules of Markovnikov and others. It is also necessary to note the differences which exist between the halides of metals of different groups, in their capacities for exchange with organic halogen derivatives and free halogens. Table 59 gives a list of the exchange reactions which have been studied in a number of systems, which shows that for none of the halides of univalent metals studied – KBr, KCl, KI, NaCl, NaBr, NaI, AgBr, AgI, etc. – could any appreciable halogen atom exchange be detected in the experimental conditions used. The same applies to most of the bivalent metal halides studied – $CdBr_2$, $MgBr_2$, $CuBr_2$, $ZnBr_2$, $MnBr_2$. However, some deviations are met here. For example, in the case of $FeBr_2$ data were obtained which clearly indicate that exchange occurs in the reactions $FeBr\overset{*}{Br} + C_2H_5Br$; $FeBr\overset{*}{Br} + \overset{*}{Br}_2$ and $FeBr\overset{*}{Br} + HBr$. Similarly, zinc bromide and manganese bromide completely dissolved in a mixture of liquid bromine and absolute alcohol, exchange extremely slowly with molecular bromine and do not exchange at all with organic halides in these conditions.

In passing to halides of metals with the highest valencies such as $CeBr_3$, $CeBr_4$, Fe_3Br_8, we find complete exchange of the atoms of these halides both with Br_2 atoms and with organic aliphatic halides. It is interesting to note that the ability of a halide to exchange its atoms increases in parallel with its ability to act as a carrier-catalyst. Apparently here, as in the case of aluminum bromide, we have anomalous mobility of the atoms within the lattice and within the molecule. HBr exchanges even with Al_2Br_6 with difficulty [211].

We show here, in somewhat simplified form, the Table 60 mentioned in the above extract, which proves that all the bromine atoms participate in the exchange of all the di- and tribromides studied.

A logical continuation of our work on the isotopic exchange of radioactive bromine between inorganic and organic bromides is the work of Fairbrother [212], in which some of the systems studied by us were investigated again, and the exchange of a large number of inorganic bromides not investigated by us with certain alkyl and

TABLE 60

Bromine Exchange of Di- and Trisubstituted Alkyl Halides with Aluminum Bromide, from the Data of Table 59

Isotopic exchange reaction	Ratio of specific activities of aluminum bromide and organic bromides at equipartition		
	Δ experimental	Δ calculated for participation of all the bromine atoms of the alkyl bromide in the exchange	Δ calculated for participation of one bromine atom of the alkyl bromide in the exchange
$CHBr_3 + AlBr_2Br^{82} \rightarrow$	0.53	0.73	2.23
$\rightarrow CHBr_2Br^{82} + AlBr_3$	0.54	0.45	1.85
$C_2H_4Br_2 + AlBr_2Br^{82} \rightarrow$	0.62	0.72	1.43
$\rightarrow C_2H_4BrBr^{82} + AlBr_3$	0.64	0.83	1.69
$C_3H_6Br_2 + AlBr_2Br^{82} \rightarrow$	0.62	0.47	0.95
$\rightarrow C_3H_6BrBr^{82} + AlBr_3$	0.79	0.80	1.62

aryl bromides was also studied. As in our experiments, aluminum bromide was found to have outstanding exchange capacity, while potassium bromide and calcium bromide practically did not exchange at all. Phosphorus pentabromide practically did not exchange in Fairbrother's experimental conditions. Tertiary butyl bromide and benzyl bromide exchanged rapidly (although more slowly than with $AlBr_3$) with $SbBr_3$, $AsBr_3$, $InBr_3$, $ZnBr_2$, $HgBr_2$ and $CuBr_2$. None of these bromides, or aluminum bromide, exchanged to any practical extent with phenyl bromide. This entirely agrees with our findings concerning the greatly reduced exchange capacity of bromine in the aromatic nucleus. A new discovery was the high exchange capacity of bromine linked to tertiary carbon, found in the exchange with the slowly exchanging stannic bromide. Tertiary butyl bromide exchanges considerably more rapidly than ethyl bromide. A similar difference of exchange rates was also found between benzyl bromide and ethyl bromide. The author considers that these results confirm the ionic mechanism postulated in his earlier papers [212b] on the Friedel–Crafts–Gustavson reaction. By this mechanism, aluminum halides commence the reaction by removal of halogen from RHal with formation of a carbonium ion R^+.

$$\mathrm{RHal} + \mathrm{AlHal_3} \rightarrow \mathrm{R^+} + \mathrm{AlHal_4^-}. \tag{158}$$

It is regarded as established in organic chemistry that a tertiary carbon is more electropositive than a secondary, and still more so than a primary: It is known that the phenyl group exerts an electrophilic action on hydrogen attached to an adjacent carbon atom, and therefore both branching of the carbon chain, and substitution of one of the hydrogens by a phenyl group should increase the polarity of the C–Hal bond.

In the carbonium exchange mechanism postulated by Fairbrother, a consequence of the increased polarity of this bond will be an increase in the value of the equilibrium constant for the reaction

$$\begin{gathered}\mathrm{RBr} + \mathrm{MeBr_3} \leftrightarrows \mathrm{R^+} + \mathrm{MeBr_4^-};\\ K = \frac{[\mathrm{R^+}]\,[\mathrm{MeBr_4^-}]}{[\mathrm{RBr}]\,[\mathrm{MeBr_3}]}\end{gathered} \tag{159}$$

Rapid isotopic exchange is also possible with small values of K if the equilibrium is established sufficiently rapidly, i.e., if the dissociation rate constant is sufficiently high. At high values of K side reactions occur, including the removal of hydrogen bromide from RBr with formation of an olefin.

Other authors have also postulated a carbonium mechanism for the isotopic exchange of halogens in organic halides. In view of the high electrophilicity of halogens, and the consequent strong polarity of the C–Hal bond, such a mechanism is more probable for halogen exchange than for hydrogen exchange, as the average life of R^+ and its equilibrium concentrations should be considerably greater for halides than for hydrocarbons. Thus, the qualitative observations of the isotopic exchange of halogens in organic compounds are explained by an association polyhalide mechanism in some cases and by a carbonium dissociation mechanism in others.

Further development of our concepts on the mechanism of exchange in organic halides involves a quantitative study of the kinetics of isotopic exchange, one expression for which is the equation

$$-\ln(1-F) = \frac{[A]+[B]}{[A]\,[B]}\,R\cdot t. \tag{160}$$

The exponential nature of isotopic exchange of organic halides with aluminum bromide was demonstrated even in our publications of the 1930's. At that time the activation energy E_{obs} = 11 kcal/mole was determined for the exchange of $AlBr_3$ with EtBr in carbon disulfide solutions. Analogous results were also obtained at that time for isotopic exchange of organic halides in aqueous solutions with halide ions and with halogens in the molecular form. All these investigations were carried out in solutions. The kinetics of isotopic exchange of halogens in organic halides in the gas phase has been studied much less. It was shown in Chapter II that when R depends on the power of [A] and [B], $R = k \cdot [A]^{\alpha} \times [B]^{\beta}$, the observed dependence of $\ln(1-F)$ on the concentrations of the exchanging molecules is expressed by the equation

$$-\ln(1-F) = k\,\{[A]+[B]\}\,[A]^{\alpha-1}[B]^{\beta-1}t. \tag{160a}$$

It is often necessary to choose between an association and a dissociation mechanism for isotopic exchange of halogens. In the first case the rate-determining stage will be the formation of an addition complex containing undissociated molecules of A and B.

Here

$$R = k\,[A]\,[B] \tag{161}$$

and

$$-\ln(1-F) = k\,\{[A]+[B]\}, \tag{162}$$

i.e., the value of the experimentally observed constant

$$k_{obs} = r = k\left\{[A]+[B]\right\}$$

depends only on the total concentration of [A] + [B]. If this sum remains constant, k_{obs} should also remain constant for any variation of the ratio [A]/[B]. The situation should be different with a semidissociative mechanism. In this case one of the two exchanging substances, for example A, dissociates reversibly according to the equation

$$A \rightleftarrows A_1 + A_2 + \ldots A_n. \tag{163}$$

Neglecting side reactions, we may assume

$$[A_1] = [A_2] = [A_3] = [A_n]. \tag{164}$$

In this case, at low degrees of dissociation, the equilibrium concentration of any i-th dissociation product may be written as

$$[A_i] \approx \frac{[A]^{1/n}}{K^{1/n}}, \tag{165}$$

where K is the appropriate dissociation constant.

With extensive dissociation, the initial constant value of [A] in Equation (165) must be replaced by some value $[A'] = [A] - \frac{1}{n}\Sigma[A_i]$. Finally, at complete dissociation the concentration of any i-th product is practically equal to [A] or to 2[A], 3[A] etc., respectively.

Let us consider exchange in which the determining stage is interaction of A_i with B.

At complete dissociation into n similar parts, of which only A_i participates in the exchange,

$$R = k[B][A_i] = k'[B][A]; \tag{166}$$

and at low reversible dissociation

$$R = k[B][A]^{1/n}\frac{1}{K^{1/n}} = k'[B][A]^{1/n}, \tag{167}$$

which gives

$$-\ln(1-F) = k_{obs}\,\{[A]+[B]\}[A]^{\frac{1}{n}-1}. \tag{168}$$

In the particular case when n = 2

$$R = k'[B][A]^{1/2}. \tag{169}$$

Equation (169) for the exchange rate R is applicable to many exchange reactions of organic bromides and iodides in different solvents, the rate being proportional to the first power of the alkyl halide concentration and the square root of the halogen concentration

$$R = k[\mathrm{RHal}]\cdot[\mathrm{Hal_2}]^{1/2}. \tag{170}$$

This is shown, incidentally, by the summary of quantitative data in the Tables of Chemical Kinetics for Homogeneous Reactions published by the U.S. Bureau of Standards [213], from which we shall quote two examples: 1) the exchange of isopropyl bromide in 90% acetone with bromine obeys Equation (169) at 25-75° with an observed activation energy E_{obs} = 23 kcal/mole [214]

$$(\mathrm{CH_3})_2\mathrm{CHBr} + \mathrm{Br}\overset{*}{\mathrm{Br}} \rightarrow (\mathrm{CH_3})_2\mathrm{CH}\overset{*}{\mathrm{Br}} + \mathrm{Br_2}; \tag{171}$$

) the exchange kinetics of trans-diiodoacetylene CHI = CHI with iodine in decalin at ≈100°C follows a similar kinetic law with E_{obs} = 26 kcal/mole [215].

In view of the appreciable dissociation of bromide and iodine in solution into atoms, it is natural to assume in these two and in similar cases that the exchange proceeds by a semidissociative molecular-atomic mechanism. This is confirmed by the accelerating action of light, which is absorbed by halogen solutions with dissociation of the halogens. The probable exchange scheme consists of three stages:

$$1)\ \mathrm{Hal}\overset{*}{\mathrm{Hal}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Hal} + \overset{*}{\mathrm{Hal}};\ \text{equilibrium constant}\quad K_1 = \frac{k_1}{k_{-1}}.$$

$$2)\ \mathrm{RHal} + \overset{*}{\mathrm{Hal}} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (\overset{*}{\mathrm{Hal}}\ldots\mathrm{RHal}) \rightarrow \mathrm{R}\overset{*}{\mathrm{Hal}} + \mathrm{Hal};\ w_2 = k_2[\mathrm{RHal}][\overset{*}{\mathrm{Hal}}].$$

$$3)\ \mathrm{Hal} + \mathrm{Hal} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{Hal_2};\ \text{equilibrium constant}\quad K_3 = \frac{k_3}{k_{-3}}.$$

No sufficient data are available at present on the more precise nature of the intermediate complex shown in parentheses in the second stage.

In photochemical exchange, light produces an increased content of free halogen atoms. Atoms are not consumed in the exchange, and therefore in ideal conditions a new photochemical equilibrium is established under irradiation, with an equilibrium constant.

$$K_1^{h\nu} > K_1, \tag{172}$$

which increases proportionately to the square root of I, which is the energy of absorption of actinic light. Since $K_1 = \frac{k_1}{k_{-1}}$ and k_{-1} should not change during irradiation, the action of light in photochemical exchange is seen in

an increase in k_1, which can often be represented by the equation

$$k_1^{h\nu} = k_1 + \alpha I^{1/2}. \tag{173}$$

Other conditions are possible, when the dissociation is non-equilibrium, and the atoms produced by the action of light are mainly consumed in some side process, such as formation of HHal. In these conditions the exchange acquires a chain mechanism, and the lower limit of the chain length can be determined from the quantum yield.

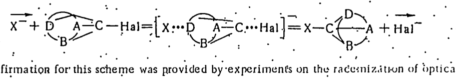
Extensive material has been accumulated on the exchange of organic halides with easily ionized inorganic halides. It is not difficult to find single and mixed solvents in which alkyl halides and alkali metal halides are soluble simultaneously. In most such solvents alkali metal halides dissociate practically completely into ions. Long before research with tagged halogens began, the kinetics of various substitution reactions of halogens in organic compounds, of the type

$$\mathrm{RHal} + \mathrm{X^-} \rightarrow \mathrm{RX} + \mathrm{Hal^-}, \tag{174}$$

where X is another halogen (for example, bromine or chlorine in iodine substitution) or a hydroxyl ion, nitrate ion, etc., had been thoroughly studied.

Extensive experimental material on the kinetics of reactions of this type has been collected and theoretically analyzed in the well known monographs by Moelwyn-Hughes [47] and Ingold [60].

If the radical R in the halide involved in a substitution reaction of type (174) is optically active, the reaction is, as a rule, accompanied by a change in the sign of optical rotation (Walden inversion). The first, though unsuccessful, attempt to correlate this change of rotation with the spatial mechanism of substitution was made by Werner [216]. A review of the material which had accumulated before application of the intermediate complex theory to these processes is contained in A. Uspensky's review [217] and in G. Wittig's monograph [218]. The first correct explanation of the Walden inversion on the basis of the statistical and quantum-mechanical theories of the intermediate complex was given by Meer and Polanyi [219], who postulated reversal of the tetrahedron (see §6 of this chapter). It must be remembered that the reason for this is the advantage, from the energy standpoint, of entry of a substituent group of the same sign from the opposite side. First an intermediate complex is formed, with a completely symmetrical arrangement of the exchanging groups. when the previously bound group is ejected in the form of an ion, this complex inevitably assumes an inverted spatial configuration, as shown below:



(175)

Direct confirmation for this scheme was provided by experiments on the racemization of optically active organic iodides [220] and fluorides, chlorides, and bromides [221] by the action of free anions of the same halogens in solutions, i.e., of F⁻ ions for RF, Cl⁻ ions for RCl, etc. The authors demonstrated that the inversion mechanism by the catalytic action of "own" ions was the same in substitution as in racemization, by comparison of the ratio of the rate of "catalytic" racemization to the rates of substitution in the reaction scheme given in Table 61

TABLE 61

Comparative Reaction Scheme, after Bergmann, Polanyi, and Szabo [221]

Organic halide	Inorganic anion			
	F^-	Cl^-	Br^-	I^-
Fluoride	Racemization	Substitution	Substitution	Substitution
Chloride	Substitution	Racemization	" "	" "
Bromide	" "	Substitution	Racemization	" "
Iodide	" "	" "	Substitution	Racemization

The comparative results for one group of reactions according to this scheme are given by the table for the rate constants of reactions methylbutylmethane halides with sodium iodide (Table 62).

TABLE 62

Rate Constants for Exchange in Anhydrous Acetone at 50°C, after Bergmann, Polanyi and Szabo [221] (Concentration $[I^-]$ 0.3 mole/liter)

Substance	k, liter · sec^{-1} · $mole^{-1}$
$CH_3C_4H_9HCF$	$1.3 \cdot 10^{-7}$
$CH_3C_4H_9HCCl$	$1.2 \cdot 10^{-5}$
$CH_3C_4H_9HCBr$	$7.4 \cdot 10^{-3}$
$CH_3C_4H_9HCI$	$1.4 \cdot 10^{-1}$

Table 62 clearly shows a regular decrease of k from RI to RI through RCl and RBr, i.e., down the last column of Table 61. The racemization rates do not show any systematic deviations from the natural sequence also if the rates are compared along other vertical columns or horizontal rows of Table 61. This is a serious argument in favor of the common nature of the substitution mechanism with optical inversion and "catalytic" racemization under the action of free ions of the same halogen.*

According to the Polanyi scheme, racemization in this case occurs as the result of substitution of some halogen atoms by others, i.e., as the result of a process identical in mechanism with isotopic substitution. Because of lack of suitable isotopes, it was not possible in 1932 to verify directly the suggested mechanism and its consequences. This was done, soon after the discovery of radioactive halogens, by a group of British scientists who studied isotopic exchange of several optically active halides with their ions in solutions [222, 223]. Study of the exchange showed that the kinetic equations which take the characteristics of isotopic exchange into account are identical for isotopic exchange and for racemization, while the numerical values of the rate constants practically coincide. This is clear from Table 63.

TABLE 63

Comparison of Rate Constants of Optical Inversion (Measured by Racemization) and Exchange for Certain Halides in Aqueous Acetone, after Hughes et al.

Reaction	$k_{opt\,inver} \cdot 10^5$	$k_{isot\,subs} \cdot 10^5$	Note
$(CH_3)(COOH)HCBr + \overset{*}{Br}^-$	5.24 ± 0.05	5.15 ± 0.50	Different systems compared at different temperatures; k in $mole^{-1}$ · liter · sec^{-1}
$(CH_3)(C_2H_5)HCI + \overset{*}{I}^-$	2.88 ± 0.03	3.00 ± 0.25	
$(CH_3)(C_6H_5)HCBr + \overset{*}{Br}^-$	3.18 ± 0.05	3.49 ± 0.37	

In view of the different accuracies of the optical and the radiometric determinations, the agreement must be considered excellent.

The results of numerous subsequent researches carried out by different workers up to 1951 are given in the article by Myers and Prestwood [22] and in reference tables [213]. We give here, in shortened form, a table from the former publication, in which data on isotopic exchange of certain organic halides, based on the equation $R = k[RHal][Hal^-]$, are uniformly, even if at times somewhat arbitrarily, presented. A careful examination of Table 64 reveals a great similarity with the laws for the exchange of $MeHal_3$ with organic halides, studied by us. The exchange rates are almost constant within a homologous series. Only the first members of such series (CH_3I in Table 64) show greatly increased reactivities.

It is clear from the table that the rate of isotopic exchange of Hal^- with RHal, for normal aliphatic halides, diminishes with increasing numbers of carbon atoms in the radical (see, for example, the series CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9). We found a similar relationship previously for the exchange of RHal with $AlHal_3$. This is not a strict law, in particular, k is somewhat higher for $C_5H_{11}I$ than for C_4H_9I.

A similar decrease of the rate with increasing R was found by other authors in the substitution of halogens by an ionic–molecular mechanism.

The decrease of k with increased degree of substitution of the carbon linked to Hal is very pronounced. This can be easily seen by comparing k for the exchange of normal and isopropyl iodides in ethyl alcohol, of normal and tertiary butyl bromides in ethylene glycol diacetate, etc. The exchange rate of bromides is considerably higher than that of chlorides; thus, k for p-nitrobromobenzene is 1740, and for p-nitrochlorobenzene it is only 0.95. It appears that iodides, in turn, exchange more rapidly than bromides, but the data for Br and I cannot be compared quantitatively because of the different solvents. In this case, the data of Neiman and his associates are more definite.

---

*As in original – Translator

TABLE 64

Rate Constants and Activation Energies for the Isotopic Exchange of Certain Organic Halides with Hal^-, after Myers and Prestwood [22]

RHal	Solvent	$k \cdot 10^{-5}$, liter · $mole^{-1}$ · sec^{-1} at 25°C	Activation energy, kcal/mole
CH_3I	Ethyl alcohol	>400	<16.5
C_2H_5I	" "	17.4 ± 0.6	22.3 ± 1.7
	" "	17.5 ± 0.4	21.3 ± 0.5
n-C_3H_7I	" "	14.0 ± 1.0	18.4 ± 0.3
		13.2 ± 1.0	20.4 ± 0.4
iso-C_3H_7I	" "	0.62 ± 0.10	21.2 ± 0.7
		0.40 ± 0.10	24.8 ± 0.8
n-C_4H_9I	" "	9.8 ± 0.3	18.4 ± 0.2
iso-C_4H_9I	" "	1.28 ± 0.06	18.8 ± 0.4
sec-C_4H_9I	" "	0.74 ± 0.06	21.8 ± 0.5
n-$C_5H_{11}I$	" "	12.0 ± 1.0	18.6 ± 0.5
n-C_3H_7Br	Acetone	3.7 ± 0.2	18.6 ± 0.4
iso-C_3H_7Br	" "	0.12 ± 0.01	23.5 ± 0.9
n-C_4H_9Br	" "	3.3 ± 0.3	18.9 ± 0.2
iso-C_4H_9Br	" "	0.14 ± 0.007	22.4 ± 0.4
p-$O_2NC_6H_4CH_2Br$	" "	1740 ± 180	18.0 ± 0.8
p-$O_2NC_6H_4CH_2Cl$	" "	0.95 ± 0.09	20.8 ± 0.7
n-C_4H_9Br	" "	106 ± 4	18.4 ± 0.5
iso-C_3H_7Br	Ethylene glycol diacetate	0.028 ± 0.004	19.9 ± 0.3
n-C_4H_9Br	" "	1.07 ± 0.03	18.2 ± 0.3
tert-C_4H_9Br	" "	~0.07	~23
2,4-$(NO_2)_2C_6H_3Br$	" "	~0.03	19.3 ± 0.5
$CH_3-CHBr-COOH$	0.5 M H_2SO_4	0.5	20.9 ± 0.5

The observed variations of k cannot be explained by changes of E. Any tendency seen in the last column is rather the reverse – to a decrease of E_{obs} with decreasing k. This indicates that the preexponential entropy factor is involved. The decrease of the rate in the transition to organic halides with halogen in the nucleus is even greater than was found by us for exchange with $AlBr_3$ (see Table 59). In the present instance the exchange with Hal^- ions is so slow that its rate constants cannot be measured. Myers and Prestwood attribute the deviations from the simple relationships between chemical structure and isotopic exchange rate, which are observed in some individual cases, to the existence of other mechanisms. In particular they postulate a mechanism different from that proposed by Meer and Polanyi for the exchange of allyl iodide and of tertiary butyl halides. In the latter case exchange by way of dissociation of RHal molecules into ions, i.e., by a carbonium mechanism, is postulated.

Other accidental causes of deviations from simple relationships are possible in comparisons of data obtained by different authors, and in recalculations without the use of the primary data. Therefore a quantitative comparison of exchange kinetics carried out by the same working group, using uniform experimental techniques and uniform theoretical treatment of the results, would be of special interest. These requirements are to some extent satisifed by the series of investigations published in recent years by M.B. Neiman and his associates. Most of these experiments were performed in 90% ethanol solution. The reaction kinetics was studied in detail for the exchange of propyl bromide with sodium bromide [224]. The authors analyzed the dependence of R on [RHal] and [MeHal] for molecular, molecular-ionic, and purely ionic, carbonium mechanisms, taking activity coefficients into account. The equation retains its usual form for molecular exchange. For the molecular-ionic and purely ionic mechanisms additional factors appear in the equation, which takes the forms:

for the purely ionic mechanism

$$k = -\frac{[B]}{([A]+[B]) \cdot t} \ln(1 - F) \qquad (176)$$

and for the molecular ionic

$$k' = ka = -\frac{1}{\{[A]+[B]\}\cdot t}\ln(1-F), \qquad (177)$$

where a is the activity coefficient. It is clear from this formula that, for the second mechanism, the experimentally observed values of k are in reality ka. Calculations based on formula (176) did not give satisfactory results. Introduction of the activity coefficients, determined from conductivity data, makes the values of k constant, as Table 65 shows. This table contains values of k for four values of [NaBr] obtained in experiments at 75°C. In columns 3 and 4 the electrochemically determined values of a are compared with the values by which k has to be divided to make its values constant. If deviations from ideal solutions are taken into account, it is clear that Equation (177), which represents an ionic–molecular mechanism, is the more suitable.

TABLE 65

Determination of the Activity Coefficient of NaBr from Kinetic Data, after M.B. Neiman et al. [224]

NaBr concentration, mole/liter	k from Equation (177)	a	
		from rate constant	from electrical conductivity
0.01	62	0.85	0.94
0.1	52	0.71	0.71
0.6	34	0.47	0.48
1.0	28	0.38	0.41

The mechanism was determined because the deduction made in an early publication [225], that activity coefficients of nonideal solutions can be determined from the relationship between the exchange rate constant and the solution concentration, was applied. With a 10-fold increase in the medium concentration region, the corrections (0.01-0.1) introduced by the activity coefficients are not large. They increase rapidly with further increase of concentration.

Equation (177) was used as the basis for calculation of k and E in all the other cases also. A separate publication gives the results of a comparison of the kinetic constants for the exchange of the first three aliphatic bromides and iodides [226]. Here we give a summary table for the rate constants.

TABLE 66

Isotopic Exchange Rate Constants $k\cdot10^5$ liter/mole · sec, after M.B. Neiman, Yu.M. Shapovalov and V.B. Miller [226]

T, °C	Reaction	Radical R		
		CH_3	C_2H_5	C_3H_7
50	$RBr + \overset{*}{Br}^-$	200	17	14
20	$RI + \overset{*}{I}^-$	630	13	10

This table indicates the existence of two rules: 1) k diminishes with increase of the number of C atoms in the radical– greatly between methyl and ethyl and slightly between ethyl and isopropyl. (In subsequent members of the series differences of k between immediate neighbors should be difficult to detect.) 2) Iodides exchange considerably more rapidly than bromides. Indeed, although in Table 66 the temperature at which the iodides are compared is 30° lower than that for the bromides, the exchange rate constant for methyl iodide is 3 times that for methyl bromide, while for the two other iodides it is only 20-30% less than for the corresponding bromides. At 50°C the rate constants for the iodides should be respectively 45, 17, and 17.5 times those for the corresponding bromides. In this respect M.B. Neiman's results confirm the conclusions of earlier investigations.

The results of a study of the influence of an increase of the number of halogen atoms in the molecule are new. Bromo- and iodosubstituted methanes were studied. In both series the exchange rate constants diminish consecutively from monosubstituted to di- and trisubstituted derivatives; i.e., while at least one hydrogen atom remains an increase of the number of Hal atoms lowers the reactivity. Fully substituted CBr_4 and CI_4 molecules, however, have considerably higher exchange capacities [227]. The authors attribute this to a different, ionic mechanism for tetrasubstituted methanes, and support this explanation by a comparison of the constancies of the constants calculated from Equations (176) and (177). The results of this comparison for the $CBr_4 + \overset{*}{Br}^-$ exchange are given in Table 67.

TABLE 67

Determination of the Mechanism of Carbon Tetrabromide Exchange from Constancy of the Values of Rate Constants in Equations (176) and (177)

[A]	[B]	Exchange rate constants $k\cdot10^5$	
		from equation (176)	from equation (177)
0.5	0.5	0.84	8
0.9	0.1	1.2	17
0.99	0.01	0.9	90

Fig. 55 and Table 68 show that the principal reason for retardation of the exchange with increasing halogen content is an increase of the activation energy.

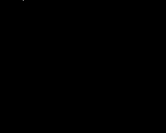


Fig. 55. Variation of the activation energy for the ionic reaction of isotopic exchange, with the number of bromine atoms in the series $CH_{4-n}Br_n$ [227].

Among the other results of this series of investigations we may mention the decrease of exchange rate with increasing substitution of hydrogen by methyl groups, and the activating effect of the double bond. In the cases of bromine and iodine CH_3Hal exchanges more rapidly than CH_3CH_2Hal, and the latter exchanges more rapidly than $(CH_3)_2CHHal$. Propylene bromide, $CH_2=CH\cdot CH_2Br$, exchanges more rapidly than propyl bromide, etc. In such cases, according to Neiman et al., the changes of k are determined mainly by changes of E. No such simple relationship exists between k and E for the isotopic exchange of the first members of the monoalkyl halide homologous series.

Table 69 shows that the rate constants decrease regularly with increasing chain length.

However, such simple relationships cannot be established by calculation of the activation energies and entropies of the process. This is seen in Table 70, which gives the values of E and ΔS for six reactions. ΔS is the entropy of formation of the intermediate complex.

According to Table 70, entropy changes are at least as significant as changes of E. In particular, in the case of methyl iodide the higher reactivity of iodides is caused by a lower value of E, and for ethyl and propyl iodides by a smaller increase of entropy, as the activation energy is greater for C_2H_5I and C_3H_7I than for the corresponding bromides. Because of the large number of misprints in the paper under discussion and of the lack of complete agreement between the graphs and tables, it is not clear how conclusive the figures in the tables are. Among other results of this series we may note a 20 to 25-fold decrease of exchange rate in passing from propyl iodide to isopropyl iodide, with very similar values for the activation energy [228]. These results are in good agreement with the earlier data of McKay [229] and of Seelig and Hull [230].

All the foregoing data refer to exchange of halide ions with alkyl halides. By irradiation of solutions of halogens in alkyl halides with actinic light, the same authors studied isotopic exchange of halogen atoms with organic halides [228]. The rate of the process is proportional to $\sqrt{I}$ where I is the light energy absorbed by the solution. This indicates an atomic mechanism. The following scheme is postulated for it:

TABLE 68

Complete Expression for the Isotopic Exchange Rate Constants of Iodine Derivatives of Methane, after Neiman et al.

RI	k, liter · mole^{-1} · sec^{-1}
CH_3I	$10^9 \exp(-15400/RT)$
CH_2I_2	$10^{10} \exp(-21700/RT)$
CHI_3	$10^{10} \exp(-22360/RT)$

TABLE 69

Isotopic Exchange Rate Constants for Bromine and Iodine Derivatives, at 100°C, after Neiman et al.

	k · 10^5 liter · mole^{-1} · sec^{-1}	
	Br	I
CH_3	5,420	120,000
C_2H_5	549	17,500
C_3H_7	403	10,000
iso-C_3H_7	11.5	1,000
CH_2Hal	2.5	230
$CHHal_2$	1.9	120

TABLE 70

E and ΔS for the Exchange of Organic Bromides and Iodides with $\overset{*}{Br}^-$ and $\overset{*}{I}^-$, after Neiman et al. [226]

Alkyl halide	E, cal/mole	−ΔS, cal/mole · degree
Methyl bromide	17,500	19.5
Ethyl bromide	18,000	22.7
n-Propyl bromide	18,400	22.0
Methyl iodide	15,400	19.5
Ethyl iodide	19,000	17.4
n-Propyl iodide	19,300	13.3

$$\left.\begin{aligned} &\dot{\mathrm{Hal}}_2 + h\nu \xrightarrow{k_1} 2\dot{\mathrm{Hal}};\\ &\dot{\mathrm{Hal}} + \mathrm{R}\dot{\mathrm{H}}\mathrm{al} \xrightarrow{k_2} \dot{\mathrm{R}} + \mathrm{Hal}\dot{\mathrm{H}}\mathrm{al};\\ &\dot{\mathrm{R}} + \mathrm{Hal}_2 \xrightarrow{k_3} \mathrm{RHal} + \mathrm{Hal};\\ &\mathrm{Hal} + \mathrm{Hal} \xrightarrow{k_4} \mathrm{Hal}_2. \end{aligned}\right\} \quad (178)$$

The kinetic relationships between reactivity and composition and structure are, in a sense, reversed for this photochemical exchange which follows an atomic chain mechanism. For example, increase of halogen atoms in the molecule increases exchange rates; the same result is produced by substitution of hydrogen by methyl radicals and by transition from normal to iso-radicals. The opposing effects of the same factors on rates of isotopic exchange by the ionic and atomic mechanisms are clearly illustrated in Table 71.

We also quote, from Yu.M. Shapovalov's dissertation, a comparison of the photochemical exchange rates of normal and isopropyl iodides with iodine at 100°C (Fig. 56). No dark reaction occurs at all. It is clear that carbon chain branching increases exchange reactivity.

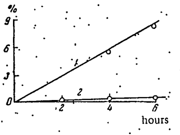


Fig. 56. Comparison of the rates of photochemical isotopic exchange of isopropyl iodide (1) and n-propyl iodide (2) with iodine under identical conditions. The ordinates represent the percentage conversion [231].

In concluding this discussion of the isotopic exchange of organic halides, we must point out that we have dealt only with the commonest and simplest mechanisms and did not consider numerous side and complicating reactions. For example, in considering exchange in solutions, we did not take into account the possibility of exchange by way of chemical reactions involving the solvent. Nevertheless, in hydroxylic solvents, such as water or alcohols, hydrolytic exchange is possible according to the scheme

$$\left.\begin{aligned} &\mathrm{RHal} + \mathrm{OH}^- \rightarrow \mathrm{ROH} + \mathrm{Hal}^-;\\ &\overset{*}{\mathrm{Hal}} + \mathrm{ROH} \rightarrow \mathrm{R}\overset{*}{\mathrm{Hal}} + \mathrm{OH}^-. \end{aligned}\right\} \quad (179)$$

In water, hydrolytic reactions of the type

$$\left.\begin{aligned} &\mathrm{Hal}_2 + \mathrm{HOH} \rightarrow \mathrm{HHalO} + \mathrm{H}^+ + \mathrm{Hal}^-\\ &\mathrm{Hal}_2 + \mathrm{OH}^- \rightarrow \mathrm{HHalO} + \mathrm{Hal}^- \end{aligned}\right\} \quad (180)$$

TABLE 71

Comparison of the Effects of the Same Factors on the Exchange of Ions and Atoms with RI [227]

RI	Atomic exchange, k, hour^{-1}	Ionic exchange, $k_{100°}$
CH_3I	0.02	1,200
CH_2I_2	34.0	2.3
CHI_3	114.0	1.2
CH_3I	0.02	12,000
CH_3CH_2I	0.04	175
$(CH_3)_2CHI$	1.6	10
$CHCH_2CH_2I$	0.056	100

may play a part in the exchange of free halogens, when the Hal⁻ ions formed can exchange with $R\overset{*}{Hal}$ or with the previously introduced halide ions. Such mechanisms have been postulated for the exchange

$$\mathrm{Hal}_2 + \overset{*}{\mathrm{Hal}}{}^- \rightarrow \mathrm{Hal}\overset{*}{\mathrm{Hal}} + \mathrm{Hal} \quad (181)$$

Of all the halogens, they are most probable for chlorine. However, even in this case, as Halford [232] showed, the main mechanism is associative exchange with intermediate formation of $(\overset{*}{Cl}_2Cl)^-$ ions. Le Roux and Sugden [233], who varied the solution pH in wide limits in the exchange of butyl iodide with lithium iodide, showed that hydrolytic mechanisms are not applicable here. pH variations from 1.3 to 7.0 at some temperatures, and from 7.6 to 12.7 at others, did not appreciably change the rate constants, while in exchange involving OH⁻ ions an increase of k, approximately proportional to the OH⁻ ion concentration, i.e., by many orders of magnitude, would be expected. However, such mechanisms cannot be completely excluded, and hydrolysis plays a definite role as a complicating side process in halide exchange. As has recently been found, in the isotopic exchange of halogens contained in complex ions with free halide ions in the solution

$$[\mathrm{A}^{k+}\mathrm{Hal}_n^-]^{(n-k)-} + \overset{*}{\mathrm{Hal}}{}^- \rightarrow [\mathrm{A}^{k+}\mathrm{Hal}_{n-1}^-\overset{*}{\mathrm{Hal}}]^{(n-k)-} + \mathrm{Hal}^- \ldots \quad (182)$$

in many cases in which a dissociation mechanism had been previously assumed, in fact reversible substitution of part of the halogen in the complex by solvent molecules (aquatation) occurs

$$\left.\begin{aligned} &[\mathrm{A}^{k+}\mathrm{Hal}_n^-]^{(n-k)-} + \mathrm{S} \rightarrow [\mathrm{A}^{k+}\mathrm{Hal}_{n-1}^-\mathrm{S}]^{(n-1-k)-} + \mathrm{Hal}^-,\\ &[\mathrm{A}^{k+}\mathrm{Hal}_{n-1}^-\mathrm{S}]^{(n-k-1)-} + \overset{*}{\mathrm{Hal}}{}^- \rightarrow [\mathrm{A}^{k+}\mathrm{Hal}_{n-1}^-\overset{*}{\mathrm{Hal}}{}^-]^{(n-k)-} + \mathrm{S} \end{aligned}\right\} \quad (183)$$

This mechanism, for the exchange of $[PtBr_4]^{2-}$ with $\overset{*}{Br}^-$ ions, was postulated by A.A. Grinberg [234] as early as 1940.

§23. Mechanism of the Isotopic Exchange of Particles Forming the Internal Coordination Groups in Complexes

Studies of the isotopic exchange of radioactive halogens have played an important part in investigations of the structure and reactivity of complex compounds. Particular mention must be made now of the work of A.A. Grinberg and his school, commenced even before the war, jointly with E.M. Filippov [203]. They studied the isotopic exchange of halogens and cyanogen in the internal coordination groups of complexes of bi- and quadrivalent platinum with each other; and with free halide and cyanide ions.

Special attention was paid to the deep mechanism of the exchange and to the relationships between reactivity and structure and composition of the complexes [234]. Introduction of halide and cyanide ions into the composition of complexes, distinct from solvates in a given solvent, changes the reactivity of these ions. In some cases the main effect is caused by a decrease of concentration, when the anions which have entered the complex do not directly participate in the reaction, but figure only as producers of free anions. This thermodynamic effect can exert a direct influence both on the isotopic exchange of central ions in the complexes, and on the exchange of additional atoms which have entered the internal coordination groups of the complex, whatever the detailed exchange mechanism may be.

The effect of complex formation is different if ions and molecules which constitute the complex, or the complex as a whole, directly enter the exchange. For the isotopic exchange of central cations by direct electron transfer this second kinetic type of influence was discussed in §2. It becomes decisive for added atoms if the dissociation of the complexes is weak.

A characteristic feature of molecules constituting complexes is the intensification of their degree of protolytic dissociation under the influence of the central positive ion [234].* It may be noted that this effect forms the basis of one of the common mechanisms of the catalytic acceleration of hydrogen exchange by cations with a tendency to complex formation.

In the prewar papers cited [234, 203] it was shown that rapid exchange of bromine from $[PtBr_4]^{2-}$ and $[PtBr_6]^{2-}$ occurs with free bromide ions in solution, and also of bromine between complexes of quadri- and hexavalent platinum, and it was found that differences between the different halogen atoms could not be detected from the exchange rates. This is in agreement with the modern structural theory according to which no special fixed bonds exist in such complexes [131, 235].

Even in these early investigations the possibility was examined, in addition to the trivial dissociative mechanism, of reversible displacement by water molecules without change of the type or symmetry of the complex.

For the exchange of $[PtX_4]^{2-}$ with $\overset{*}{X}^-$ this mechanism may be represented as

$$\left.\begin{array}{l}[PtX_4]^{2-} + H_2O \rightleftarrows [PtX_3H_2O]^- + X^-;\\ [PtX_3\cdot H_2O]^- + \overset{*}{X}^- \rightleftarrows [PtX_3\overset{*}{X}]^{2-} + H_2O.\end{array}\right\} \qquad (184)$$

A combination of this equation with analogous equations for the exchange of Br^- with $[Pt(NH_3)_2Br_2]$ results in isotopic exchange of halogens from two complexes, etc. This idea was developed further in a recently published paper by A.A. Grinberg, L.E. Nikolskaya and G.A. Shagisultanova [236]. Here, in addition to substitution by solvent molecules, account is taken of further dissociation of water molecules in the complex; i.e., Equation (184) is replaced by Equation (185)

$$\left.\begin{array}{l}[PtX_4]^{2-} + H_2O \rightleftarrows [PtX_3H_2O]^- + X^-\\ [PtX_3H_2O]^- \rightleftarrows [PtX_3OH]^{2-} + H^+\\ \hline [PtX_4]^{2-} + H_2O \rightleftarrows [PtX_3OH]^{2-} + H^+ + X^-\end{array}\right\} \qquad (185)$$

Its first stage may be slow, while protolytic dissociation of intracomplex water usually occurs slowly [237]. The substitution scheme evolved by A.A. Grinberg is completed if it is postulated that the exchange proceeds through intermediate addition complexes containing more than four addends for Pt^{IV} complexes and more than six for Pt^{II} complexes, for example

$$[PtX_4]^{2-} + H_2O \rightleftarrows \underset{\substack{\text{intermediate}\\ \text{complex}}}{[PtX_4\cdot H_2O]^{2-}} \rightleftarrows [PtX_3H_2O]^- + X^-$$

$$[PtX_3H_2O]^- + \overset{*}{X}^- = \underset{\substack{\text{intermediate}\\ \text{complex}}}{\{PtX_3\cdot\overset{*}{X}\cdot H_2O\}^-} \rightleftarrows [PtX_3\overset{*}{X}]^{2-} + H_2O$$

Similar schemes have been postulated for allied systems by American authors, but they postulated the formation of stabler intermediate addition complexes with an anomalous odd number of addends. For example, Adamson et al., who made a very detailed study of the isotopic exchange of hexacyanomanganate (III) with cyanide ions tagged with C^{14}, showed that R for the exchange is independent of the ionic strength of the solution and of the cyanide ion concentration for a first order reaction with respect to the $[Mn(CN)_6]^{3-}$ concentration. These results, the fact that the exchange was independent of the solution pH, and the absolute values of the rate constants and activation energy (approximately 8.5 kcal/mole) of the exchange, led to an exchange scheme involving aquatation according to the equation

$$[Mn(CN)_6]^{3-} + H_2O \rightleftarrows [Mn(CN)_6H_2O]^{3-} \rightleftarrows [Mn(CN)_5H_2O]^{2-} + CN^- \qquad (186)$$

---

* A similar conclusion was reached somewhat later by British workers [131] who studied exchange between complex amines and heavy water.

with intermediate formation of an aqua-complex with coordination number 7. This scheme, with details of the electronic structure of the different trivalent ions taken into account, explains the sequence of the hexacyanides in order of their isotopic exchange activities

$$[Mn(CN_6)]^{3-} \gg [Cr(CN)_6]^{3-} > [Fe(CN)_6]^{3-} \approx [Co(CN)_6]^{3-}. \qquad (187)$$

For the exchange of cyanide complexes of bivalent metals, Adamson [239] also considered the intermediate formation of aqua-complexes with coordination number 5, and gives the results of magnetic and kinetic determinations which indicate the relatively high stability of complexes of this type in the case of Co^{II}, including the complex $[Co(CN)_5]^{3-}$. More symmetrical intermediate complexes with coordination number 6 (or 8) are rejected for a number of reasons.

The mechanisms postulated by Grinberg and Adamson are variations of the association mechanism, although the authors assume the possibility of a two stage substitution of X^- by water by a dissociation mechanism. The existence of such mechanisms with participation of water is demonstrated by a comparison of the rate of substitution of thiocyanate ions by water and the isotopic exchange of thiocyanate ions, studied by Adamson and Wilkins [240], and also by the increase of the exchange reactivity of $[PtBr_4]^{2-}$ complexes on standing, discovered by A.A. Grinberg and L.E. Nikolskaya [236]. This new effect is interpreted as the consequence of slow aquatation with formation of the more reactive $[PtBr_3\cdot H_2O]^-$ ions. The existence and wide occurrence of a third oxidation-reduction mechanism is proved on the basis of earlier detailed investigations of oxidation-reduction processes occurring within the complex, and of direct experiments on the detection of free halogens in complexes with high coordination numbers.

In our view, a serious argument in favor of association exchange mechanisms is the interesting relationship established by A.A. Grinberg and L.E. Nikolskaya [241] between exchange capacity and complex stability. With a dissociation mechanism, exchange should be retarded with increasing stability of the complex, because of the decreased degree of dissociation. With an association mechanism, both an increase and a decrease of the exchange rate with increasing stability of the complexes is possible. It was shown long ago by several independent methods that bivalent platinum complexes of the type $[PtX_4]^{2-}$, where X is cyanogen or halogen, form the following sequence in order of stability

$$CN^- > I^- > Br^- > Cl^-. \qquad (188)$$

Table 72 gives data on the rates and activation energies of isotopic exchange for complexes with these four anions.

TABLE 72

Comparison of Rates of the Isotopic Exchange Reactions of $[PtX_4]^{2-} + \overset{*}{X}^-$ at Room Temperature, after A.A. Grinberg and L.E. Nikolskaya [236, 241]

Anion	Concentration of complex, mole/liter	Time to reach equilibrium activity distribution, min	Exchange activation energy, kcal/mole
CN^-	$0.37\cdot10^{-1}$	5	Near 0
I^-	$1.03\cdot10^{-1}$	25	6
Br^-	$0.51\cdot10^{-1}$	40	(17)**
Cl^-	$0.72\cdot10^{-1}$	>60*	12

*Only 11% exchange occurred in 60 minutes.

**The value 17 for Br^- was kindly supplied by the author.

Although, because of its uncertainty, the time to reach equilibrium distribution of activity cannot be regarded as a successful quantitative expression of the rate, it does give some idea of the relative exchange capacity. It is clear from the table that the isotopic exchange rate increases with increasing stability of the complexes and is highest for the tetracyanide and tetraiodide, and that the increase of the rate is caused mainly by a decrease of activation energy. However, the differences between the rates are less than expected, and ΔS and k_{∞} probably increase with increasing E. Similar results were obtained by the same authors in a comparison of the stabilities and exchange capacities of hexahalides and hexacyanides of quadrivalent platinum. However, the increase of activity with stability has a limit, as is shown by the practically total absence of isotopic exchange of cyanide ions contained in ferrous and ferric hexacyanides. This is readily explained within the framework of an association mechanism. A.A. Grinberg admits the possible existence of different mechanisms, and attributes decisive importance to the rate of reversible formation and cleavage of $Me^{n+} \cdot Hal^-$ bonds. It is assumed that the bonds which are thermodynamically the most stable are also formed and broken more rapidly than the others. This is a possible consequence of the Bronsted-Polanyi relationship between E and Q.

$$E_1 = E_0 - \alpha Q. \qquad (189)$$

However, since $\alpha < 1$, in passing from one type of addend to another, it would be natural to expect changes of Q in excess of changes of E. Consequently the activation energy of the reverse reaction

$$E_2 = E_1 + Q = E_0 + (1 - \alpha) Q \qquad (189a)$$

should increase with Q, i.e., with increasing stability of the complexes. It is not clear how in these circumstances the rate constants for the forward and reverse reactions can increase simultaneously.

Thus, the origin of the interesting relationship between stability and exchange reactivity of inorganic complex ions is not yet finally decided. A.A. Grinberg emphasizes the importance, in this case, of I.I. Chernyaev's trans-influence [242], but this interesting suggestion has not yet been developed further or studied systematically.

In recent years, owing to the introduction of new physical and physicochemical methods, there has been an appreciable move in studies of the reaction kinetics of inorganic complex ions, and the systematic development of a theory which relates the reactivity of complexes to their chemical composition, the electrostatic and electronic characteristics of their constituent particles, and their spatial structure, has commenced. These questions have been considered in detail in Taube's review [235] on the rates and mechanisms of substitution reactions of inorganic complexes in solutions, extensive use being made of the results of isotopic studies. In this review the isotopic exchange rate is taken as the simplest and most direct measure of the reactivity (lability) of complexes in substitution reactions, and a wealth of experimental data is used to prove the validity of this application of isotopic exchange.

In addition to the data on the isotopic exchange of halides and cyanides with which we are already familiar, use has also been made of the results of a comparative investigation of the isotopic exchange of oxalate, present in the form of $C_2O_4^{2-}$ anions in iron, aluminum, chromium, and cobalt complexes [243] of the type $[Me^{III}(C_2O_4)_3]^{3-}$. No exchange could be detected in the last two complexes with the use of C^{11}. This does not exclude the possibility of slow exchange, with $\tau_{1/2}$ measured in hours. The exchange with analogous complexes of aluminum and iron is very rapid. Mention should also be made of the work of Harris [244] who studied the slow exchange of CO_3^{2-}, tagged with C^{14}, with $[Co(NH_3)_4CO_3]^+$.

A comparison of the data of Long, Taube, and others on the exchange of neutral water, univalent halide and cyanide ions, and bivalent oxalate ions in complexes with trivalent central cations, readily shows the very great importance of the nature of the central cation. The same particles retain a high exchange reactivity when within aluminum and iron complexes, but have low mobilities in chromium complexes. The behavior of trivalent cobalt complexes is in most cases similar to the behavior of trivalent chromium complexes. This indicates the determining importance of the electronic structure of the cation. Extensive data have accumulated in the scientific literature on isotopic exchange which confirm the validity and general applicability of this conclusion [235, 240]. A discussion of this would involve a digression into the theory of the structure of complex compounds of the transition metals, which would be outside the scope of this monograph.

§24. Classification of Isotopic Exchange Reactions

In concluding the chapter on the mechanism of isotopic exchange, we return to its classification. For orientation in the wealth of processes of various types and mechanisms, combined under the very broad concept of isotopic exchange, it is useful to define narrower groups. According to the nature of the problem, both the combination of individual processes into groups, and the combination of the latter into larger divisions and the design of a general classification may be based on different principles.

If isotopic exchange is being studied in relation to the chemistry of substances of a particular type, or in relation to the chemistry of particular elements, it is natural to base the classification on the chemical composition or the chemical functions of the exchanging compounds. From this standpoint it is possible to consider the exchange of metals and nonmetals separately, with further subdivision into groups of the periodic table and into individual elements. This principle was partially used in our consideration of hydrogen exchange, halogen exchange, etc., in individual sections. Such a classification could be augmented by formation of separate subgroups of isotopic exchange of particular types of compounds, for example, carbohydrates and organic oxygen compounds in organic chemistry, etc.

In certain cases it is useful to base the classification on the state of aggregation and the physical properties of phases, for example, by considering separately exchange in the gas, liquid, and solid phases, with further subdivision into heterogeneous and homogeneous exchange. Further, for liquids in some instances it is convenient to consider exchange separately for electrolytic and nonelectrolytic solutions, etc., and to carry the subdivision as far as individual solvents (water, ammonia, benzene, etc.). In the same way, exchange in the solid phase could be considered separately for ionic, metallic, atomic, and molecular crystals, etc.

In studies of isotopic exchange kinetics it is convenient to classify reactions into simple and complicated exchange, with differentiation of the latter according to the nature of the complications. In other cases it is more appropriate to commence with the division, considered in Chapter VI, into large classes by the type of the acting energy, with further subdivision according to the state of aggregation, heterogeneity and homogeneity, and phase composition. None of these classifications covers every aspect of the phenomenon, and attempts to make them comprehensive would only result in great complexity, which would deprive the classification of practical value. This is also valid with regard to classification of isotopic exchange according to the nature of the elementary step, which was used in the discussion in the first half of this chapter. The advantage of this classification is that the grouping is by the inner mechanisms, and not by external and phase conditions, and the fact that most of the types in exchange known at the present time can be included into the separate sections and groups.

This principle has been used in Table 73 to classify the main types of exchange known at the present time, to which certain types which have not yet been studied, but which are probable, have been added. In principle, this classification is applicable not only to the thermal reactions which have been predominantly studied, but also to reactions induced by other forms of energy (photochemical and radiochemical exchange, etc.) Each of the three classes of exchange of the chemical type (Division A) includes both homogeneous and heterogeneous processes, and both intra- and intermolecular as well as intracrystallite processes.

Intramolecular exchange is not found in the groups of Division B. Some of them also do not contain intracrystallite and intermolecular exchange, but they all include both homogeneous and heterogeneous processes. The same class in Table 73 may contain reactions with different numbers of steps and with determining steps of different types.

With any of the original mechanisms the exchange may be simple or complicated, if these terms are used in the sense explained in Chapters II and V. In addition, it is necessary to take into account the existence of intermediate types and complex cases, when the same process includes steps belonging to different classes, or exchange occurs simultaneously and independently by mechanisms belonging to different classes of the same division or even of different divisions. Finally, with any of the initial mechanisms considered, the reaction may proceed, according to conditions, with a kinetic, diffusional, or mixed regime. Thus, the sources of complications are numerous, and a clear classification is therefore particularly important. The diversity of mechanisms and complications may act as a source of difficulties in ascribing a definite type to a given process. The overcoming of these difficulties by a detailed analysis of the characteristics and conditions of the process, and of variations of the latter, is rewarded by the possibility of applying to a process for which a definite position has been found in the system, of the laws which have been established for the given group of reactions.

In the table, all isotopic exchange reactions have been divided into two types, of unequal importance and

TABLE 73

Classification of Isotopic Exchange Reactions by the Nature of the Transferred Particles

A. CHEMICAL ISOTOPIC EXCHANGE

Class I. Exchange based on electron transfer

Group	Characteristics of elementary mechanism and properties	Notes
1. Exchange between cations of the same element:		Intramolecular analogs are possible.
a) simple cations and their hydrates in aqueous solutions,	Non-adiabatic transfer by collisions, with subsequent or previous reconstruction of solvates and complexes.	
b) complex cations in aqueous solutions;	The same, by tunnel transfer.	Heterogeneous analogs are possible for all subgroups, in which electron transfer is invariably followed by ion or atom transfer.
c) simple and complex cations in nonaqueous solutions; d) exchange between simple and complex cation	The nature and stability of the solvation are important. A positive influence is exerted by electrostatic attraction, and a negative influence by electrostatic repulsion of the directly exchanging particles. Hence the wide occurrence of catalytic effects of simple anions. Sensitivity to solution pH and catalysis by "joining" ions are typical here.	
2. Exchange between polyatomic and complex anions: a) aqueous solutions; b) nonaqueous solutions.	The same types of electron transfer as in Group 1. Because of the large size of the anions, solvation and direct electrostatic interaction play subordinate roles.	Heterogeneous and intramolecular analogs are probable.
3. Exchange between ions of opposite sign.	The same types of electron transfer as in Groups 1 and 2. Electrostatic attraction facilitates the process.	Heterogeneous and intramolecular analogs are probable.
4. Exchange between ions, neutral atoms, and molecules.	The same types of electron transfer as in Groups 1, 2 and 3. The pH has a strong influence.	

Class II. Exchange based on transfer of atoms or simple monoatomic ions, without electron transfer, as the determining stage

Group	Characteristics of elementary mechanism and properties	Notes
1. Acid-base protolytic exchange: a) of inorganic molecules with solvent; b) of inorganic molecules with each other; c) of organic molecules with the solvent or with inorganic molecules; d) of organic molecules with each other.	Exchange effected by proton transfer. Nature and dielectric constant of the solvent, polarity of the H–X bond, and presence of free electron pairs are important. Very common in solutions. Absent or very rare in the gas phase; catalyzed by acids and bases.	Intramolecular and heterogeneous analogs exist.

TABLE 73 (continued)

Group	Characteristics of elementary mechanism and properties	Notes
2. Exchange between inorganic substances with cation transfer.	Found in dissociative exchange of central cations in complex ions with simple ions and with each other. Typical for solutions. Possible in melts and solids.	Question of heterogeneous and intramolecular analogs is not clear.
3. Exchange of inorganic and organic molecules by atom transfer.	Exchange effected by atom transfer, with or without intermediate dissociation. Bond strength is important. Possible in gas phase and solutions. Sensitive to the action of catalysts which induce dissociation. The exchange is often a chain process.	
4. Exchange by transfer of simple anions: a) exchange of organic substances; b) exchange of inorganic substances; c) exchange between organic and inorganic substances.	Simple anions are transferred. Both dissociation and association mechanisms are possible. Typical for exchange in solutions. Possible in melts and in the solid phase.	The question of heterogeneous analogs is not clear for a). Intramolecular analogs are possible.

Class III. Exchange based on transfer of neutral or charged particles containing two or more atoms

1. Exchange based on transfer of di-, tri-, and polyatomic anions.	Association and dissociation mechanisms are possible. Common in the chemistry of solutions of inorganic complex compounds and of organic compounds.	Heterogeneous and intramolecular analogs are possible.
2. Exchange with transfer of neutral diatomic, triatomic, and more complex radicals.	Mono- or biradicals are transferred. Association and dissociation mechanisms are possible. Exchange often a chain process.	Heterogeneous and intramolecular analogs are possible.
3. Exchange between different substances with transfer of neutral stable molecules.	Molecules without free covalent or ionic valences are transferred. Mechanism typical for exchange between phases and in complex compounds.	Heterogeneous exchange is common.

TABLE 73 (continued)

B. PHYSICOCHEMICAL ISOTOPIC EXCHANGE BETWEEN DIFFERENT PHASES AND WITHIN PHASES

Class I. Exchange with transfer of atoms, molecules, and ions

Group	Characteristics of elementary mechanism and properties	Notes
1. Exchange in evaporation of liquids and solids. 2. Exchange during solution of liquids and solids. 3. Exchange during diffusional redistribution.	The mechanism is physicochemical. Molecules, atoms, solvated ions, or ions are transferred without change of chemical state.	Heterogeneous exchange is predominant.

Class II Exchange with transfer of macromolecules, droplets, or crystallites

1. Exchange of colloidal solutions on mixing and diffusion. 2. Exchange on peptization and coagulation. 3. Exchange in aerosols, powders, etc.	Macrophysical mechanism.	Not yet studied

occurrence. The first includes processes of a chemical nature, the elementary mechanism of which is the same as in ordinary chemical reactions but unaccompanied by changes of elementary composition; the second contains reactions with different physicochemical or even macrophysical mechanisms.

The first class of the second type includes exchange of monoatomic and larger molecules and ions between phases by means of reversible evaporation and condensation, and similar exchange by means of reversible solution. It is assumed that macroscopic evaporation, condensation, solution, or crystallization, do not occur, and that the system is in a state of true or delayed equilibrium* in the usual sense of the word, apart from redistribution of isotopes. Isotopic exchange of the physicochemical type has been observed repeatedly, but no systematic studies of its kinetics have been undertaken. In the most typical extreme cases, such as the exchange between liquid mercury and mercury vapor, or between crystalline benzene and liquid benzene or solutions of benzene in other solvents, there is a clear and undoubted distinction between the chemical and the physicochemical types. However, between these extreme types intermediate cases are found, in which evaporation, solution, or diffusive displacement is accompanied by rupture or formation of chemical bonds. Such cases are difficult and sometimes impossible to allocate to one of these types.** Processes of the 2nd class of the nonchemical type of exchange have practically not been studied at all, but they undoubtedly exist and may eventually become of independent interest.

This classification has been designed for processes which occur without evident changes of chemical composition and without changes in the distribution of elements and compounds between different phases and portions of a substance. However, in its deep elementary mechanism none of the types, classes, or groups of isotopic exchange reactions differs in principle from definite types, classes, or groups of ordinary physical and physicochemical processes. Therefore the classification can also be extended to isotopic exchange which occurs simultaneously with ordinary chemical and physicochemical processes. It should be remembered, however, that with a similar or even an identical mechanism the course of isotopic exchange and of ordinary chemical and physicochemical processes may follow different kinetic laws. This must be taken into account in kinetic analysis of mixed cases.

We shall also note the special nature of the kinetic relationships and, in part, also of the mechanisms, of isotopic exchange of particles in boundary layers in interfaces; we will return to this question at the end of Chapter V.

---

*Equilibrium of the physicochemical type may be true (and the exchange complete) with respect to the phase surface, and delayed (and the exchange partial) with respect to the bulk of the phase.

**For this reason self-diffusion in solids has not been included in the system. For ionic and atomic lattices this is a special variation of isotopic exchange of the chemical type, and for molecular lattices and liquids it belongs to the physicochemical type.

LITERATURE CITED

[1] M. Haissinsky, J. Chim. Phys. 47, 957 (1950).

[2] J.W. Gryder and R.W. Dodson, J. Am. Chem. Soc. 71, 1894 (1949); 73, 2890 (1951).

[3] H.G. Hornig and W.F. Libby, J. Phys. Chem. 56, 869 (1952).

[4] J. Sheppard and A. Wahl, J. Am. Chem. Soc, 75, 5133 (1953).

[5] N. Bonner and H. Portratz, J. Am. Chem. Soc. 73, 1845 (1951).

[6] D.I. Blokhintsev, Principles of Quantum Mechanics, Ch. 16, 2nd ed., Moscow (1949).

[7] H. Pelzer, Z. phys. Chem. B15, 445 (1932); L. Farkas and E. Wigner, Trans. Far. Soc. 32, 708 (1936).

[8] S. Glasstone, K. Laidler and H. Eyring, Theory of Rate Processes, Moscow, Foreign Lit. Press (1948).

[9] V.N. Kondratyev, Structure of Atoms and Molecules, Moscow–Leningrad, Acad. Sci. USSR Press (1946).

[10] W.F. Libby, J. Phys. Chem. 56, 863 (1952).

[11] W. Biltz, Z. anorg. Chem. 164, 246 (1927).

[12] A. Mitchell and M. Zemansky, Resonance Radiation and Excited Atoms, Moscow, United Sci.-Tech. Press (1937).

[13] J. Weiss, Proc. Roy. Soc. (A) 222, 128 (1954).

[14] a) R.J. Marcus, B.J. Zwolinsky and H. Eyring, J. Phys. Chem. 58, 432 (1954); b) B.J. Zwolinsky, R.J. Marcus and H. Eyring, Chem. Rev. 55, 157 (1955).

[15] a) H. Taube and E. King, J. Am. Chem. Soc. 73, 4053 (1952); b) H. Taube and H. Myers, ibid. 76, 2103 (1954).

[16] G. Harbuttle and R.W. Dodson, J. Am. Chem. Soc. 73, 2442 (1951).

[17] H. Fromherz and K.–H. Lih, Z. phys. Chem. A153, 321 (1931).

[18] E.G. Meyer and M. Kahn, J. Am. Chem. Soc. 73, 4950 (1951).

[19] S.Z. Roginsky, Problems of Kinetics and Catalysis 8, 112 (1955).

[20] L.V. Pisarzhevsky and M.A. Rozenberg, The Electron in the Chemistry of Solutions and Electrochemistry, Ukrainian State Press (1923); L.V. Pisarzhevsky, Bull. Ekaterinoslav Mining Inst. (1918).

[21] G. Seaborg, Chem. Rev. 27, 256 (1940).

[22] O. Myers and R. Prestwood, Radioactivity Applied to Chemistry, edited by Wahl and Bonner, Moscow, Foreign Lit. Press, p. 11 (1954).

[23] L. Van Alten and C.N. Rice, J. Am. Chem. Soc. 70, 883 (1948).

[24] J.N. Northrop and M.L. Anson, J. Gen. Physiol. 12, 543 (1929).

[25] H.A. Kierstead, J. Chem. Phys. 18, 756 (1950).

[26] V.J. Linnenbom and A.C. Wahl, J. Am. Chem. Soc. 71, 2589 (1949); R.H. Betts, H.S.A. Gilmour and R.K. Leigh, J. Am. Chem. Soc. 72, 4978 (1950).

[27] R.W. Dodson, J. Am. Chem. Soc. 72, 3315 (1950).

[28] J.H. Baxendale and P. George, Trans. Far. Soc. 46, 55; 736 (1950).

[29] J. Silverman and R.W. Dodson, J. Phys. Chem. 56, 846 (1952).

[30] R.J. Prestwood and A.C. Wahl, J. Am. Chem. Soc. 71, 3137 (1949).

[31] M.H. Robertson, and G.W. Law, Trans. Far. Soc. 31, 899 (1935); M.H. Gorin, J. Am. Chem. Soc. 58, 1787 (1936).

[32] R.L. Ward and S.I. Weissman, J. Am. Chem. Soc. 76, 3612 (1954).

[33] H. Linschitz, M. Berry and D. Schweitzer, J. Am. Chem. Soc. 76, 5833 (1954).

[34] I.L. Gross, B.P. Zakharchenya and N.M. Reinov, Proc. Acad. Sci. USSR 97, 57, 221 (1954).

[35] A. Farkas, Orthohydrogen, Parahydrogen and Heavy Hydrogen, Moscow–Leningrad, United Sci.-Tech. Press (1936)

[36] W.H. Johnston and C.J. O'Shea, J. Chem. Phys. 21, 2080 (1953).

[37] W.H. Johnston and R.M. Anstett, J. Chem. Phys. 22, 146 (1954).

[38] H. Dodgen, and W.F. Libby, J. Chem. Phys. 17, 951 (1949).

[38a] W.H. Johnston and W.F. Libby, J. Am. Chem. Soc. 73, 854 (1951).

[39] G. Hevesy and L. Zechmeister, Ber. 53, 410 (1920).

[40] A.A. Grinberg and L.E. Nikolskaya, J. Appl. Chem. 22, 542 (1949); 24, 893 (1951).

[41] J. Fuck, Trans. Far. Soc. 34, 222 (1938).

[42] W. Koskoski, H. Thomas and R. Fowler, J. Am. Chem. Soc. 63, 2451 (1941).

[43] M. Haissinsky and M. Cottin, J. Chim. Phys. 46, 476 (1949).

[44] R.L. Wolfgang and R.W. Dodson, J. Phys. Chem. 56, 872 (1952).

[45] S.Z. Roginsky and N.M. Gopshtein, Phys. Z. Sow. 7, 672 (1935); N.E. Brezhneva, S.Z. Roginsky and A.I. Shilinsky, J. Phys. Chem. 9, 296 (1937); 10, 367 (1937).

[46] N.N. Semenov, Some Problems of Chemical Kinetics and Reactivity, Moscow, Acad. Sci. USSR Press (1954).

[47] E.A. Moelwyn-Hughes, The Kinetics of Reactions in Solution (Oxford, 1947).

[48] A.F. Polesitsky and F.L. Temerlin, Proc. Acad. Sci. USSR 30, 803 (1941); A. Zaidel and V. Rotshtein, Proc. Acad. Sci. USSR 57, 587 (1947).

[49] J.P. Hunt and H. Taube, J. Chem. Phys. 19, 602 (1951); A. Rutenberg and H. Taube, J. Chem. Phys. 20, 825 (1952).

[50] A.I. Brodsky, Chemistry of Isotopes, Moscow, Acad. Sci. USSR Press (1952).

[51] R.A. Ogg, J. Chem. Phys. 15, 613 (1947); 18, 572, 573 (1950).

[52] E.N. Guryanova and V.N. Vasilyeva, J. Phys. Chem. 28, 60 (1954); 29, 577 (1955).

[53a] Yu.A. Gorin, J. Gen. Chem. 16, 283 (1946); M.Ya. Kagan, G.D. Lyubarsky and O.M. Podurovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 173 (1947).

[53b] O.M. Vinogradova, N.P. Keier and S.Z. Roginsky, Summaries of Papers at the All-Union Conference on the Use of Isotopes in Catalysis, Acad. Sci. USSR Press (1956).

[54] M.M. Sakharov, Dissertation, Inst. Phys. Chem., Acad. Sci. USSR (1955).

[55] A.I. Shatenshtein, Theory of Acids and Bases, State Chem. Press (1949).

[56] A.I. Brodsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 3 (1949); J. Gen. Chem. 24, 413 (1954).

[57] G.P. Miklukhin, "Sources and Transference Routes of Hydrogen in the Reactions of Organic Compounds," Doctorate Dissertation, Inst. Phys. Chem., Acad. Sci. USSR (1954).

[58] C.K. Ingold, Chem. Rev. 15, 225 (1934); C.K. Ingold and C.L. Wilson, Z. Elektrochem. 44, 62 (1938). O. Reitz, Isotopenkatalyse in Lösungen, Handb. d. Katalyse 2, 272 (1940).

[59] D.N. Kursanov and V.V. Voevodsky, Progr. Chem. 23, 641 (1954).

[60] C.K. Ingold, Structure and Mechanism in Organic Chemistry (New York, 1953).

[61] A.N. Nesmeyanov, Annals Moscow State Univ. No. 132, 5 (1950).

[62] R.Ya. Levina, Synthesis and Contact Conversions of Unsaturated Hydrocarbons, Moscow State Univ. Press (1949).

[63] W. Nernst, Z. Elektrochem. 24, 335 (1918); J.A. Christiansen, J. Phys. Chem. 28, 145 (1924).

[64] N.N. Semenov, Chain Reactions, Leningrad, United Sci.-Tech. Press (1934).

[65] F.O. Rice and K.K. Rice, Aliphatic Free Radicals, Moscow, United Sci.-Tech. Press (1937).

[66] Y. Cario and I. Frank, Z. Phys. 11, 161 (1922); 37, 61 (1926).

[67] R.W. Wood, Proc. Roy. Soc. A97, 455 (1920); A102, 1 (1922).

[68] K.F. Bonhoeffer, Z. Phys. Chem. 113, 119, 492 (1924); Z. Elektrochem. 31, 521 (1925); Ergeb. exakt. Naturwiss. 6, 201 (1927).

[69] A.B. Shekhter, Problems of Kinetics and Catalysis, Vol. 2, Chemical Reactions in the Electric Discharge Leningrad, p. 26 (1935); I.V. Kurchatov, Problems of Kinetics and Catalysis, 2, Leningrad, p. 8 (1935).

[70] D.N. Andreev, Organic Synthesis in Electric Discharges, Moscow–Leningrad, Acad. Sci. USSR Press (1953).

[71] E.W. Steacie, Atomic and Free Radical Reactions (1954); T.G. Majury and E.W. Steacie, Disc. Far. Soc. 14, 45 (1953).

[72] K.H. Geib and E.W. Steacie, Z. phys. Chem. 13, 29, 215 (1935).

[73] K.H. Geib, Z. Elektrochem 44, 81 (1938).

[74] N.R. Trenner, K. Morikawa and H.S. Taylor, J. Chem. Phys. 5, 203 (1937).

[75] W.R. Trost, B. Darwent and E.W.R. Steacie, J. Chem. Phys. 16, 358 (1948); W.R. Trost and E.W.R. Steacie, J. Chem. Phys. 16, 361 (1948).

[76] M. Szwarc, Chem. Rev. 47, 75 (1950); M. Szwarc and J.W. Taylor, J. Chem. Phys. 22, 270 (1954).

[77] E.W.R. Steacie, Canad. J. Res. 15B, 264 (1937).

[78] C.K. Ingold, C.G. Raisin and C.L. Wilson, Nature 134, 734 (1934); J. Chem. Soc. 915 (1936).

[79] B. Darwent and R. Roberts, Disc. Far. Soc. 14, 50 (1953).

[80] A. Farkas and H.W. Melville, Proc. Roy. Soc. A157, 625 (1936).

[81] A.F. Trotman-Dickenson, J.R. Birchard and E.W.R. Steacie, J. Chem. Phys. 19, 162 (1951).

[82] F.O. Rice and E. Teller, J. Chem. Phys. 6, 49 (1938).

[83] B. Gorin, W. Kunzmann, J. Walter and H. Eyring, J. Chem. Phys. 7, 633 (1939).

[84] V.V. Voevodsky, G.K. Lavrovskaya and R.E. Mardaleishvili, Proc. Acad. Sci. USSR 81, 915 (1951).

[85] R.E. Mardaleishvili, Lomonosov Lectures, Moscow Univ. Press (1953).

[86] G.K. Lavrovskaya, Dissertation, Inst. Phys. Chem., Acad. Sci. USSR (1954).

[87] V.A. Poltorak and V.V. Voevodsky, Proc. Acad. Sci. USSR 91, 589 (1953).

[88] A.S. Fomenko and E.A. Sadovnikova, J. Phys. Chem. 22, 423 (1948).

[89] T.D. Stewart and D. Harman, J. Am. Chem. Soc. 68, 1135 (1946).

[90] R.L. Burwell and G. Gordon, J. Am. Chem. Soc. 70, 3128 (1948).

[91] G. Gordon and R.L. Burwell, J. Am. Chem. Soc. 71, 2355 (1949).

[92] C.K. Ingold, C.G. Raisin and C.L. Wilson, J. Am. Chem. Soc. 1643; 1637 (1936).

[93] A. Klitz and A. Langseth, Nature 135, 956 (1935); Z. phys. Chem. A176, 65 (1936).

[94] A.P. Best and C.L. Wilson, J. Chem. Soc. 28 (1938); C.R. Bayby and A.P. Best, Nature 139, 880 (1937); J. Chem. Soc. 255 (1946).

[95] J. Turkevich and R.K. Smith, Nature 157, 874 (1946).

[96] J. Turkevich and R.K. Smith, J. Chem. Phys. 16, 466 (1948).

[97] S.F. Birch and A.E. Dunstan, Trans. Far. Soc. 35, 1013 (1939).

[98] F. Whitmore, Symposium, "Synthesis of Motor Fuel" No. 1, Foreign Lit. Press, p. 7 (1949).

[99] F. Whitmore, J. Am. Chem. Soc. 54, 3264 (1932).

[100] R.L. Burwell, R.B. Scott, L. Maury and A.S. Hussey, J. Am. Chem. Soc. 76, 5822 (1954).

[101] R.L. Burwell, L.G. Maury and R.B. Scott, J. Am. Chem. Soc. 76, 5828 (1954).

[102] V.N. Setkina, D.N. Kursanov, O.D. Sterligov and A.L. Liberman, Proc. Acad. Sci. USSR 85, 1045 (1952).

[103] D.N. Kursanov, V.N. Setkina and O.D. Sterligov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1035 (1953).

[104] A.I. Shatenshtein, K.I. Zhdanova, L.N. Vinogradov and V.R. Kalinachenko, Proc. Acad. Sci. USSR 10[illegible], 778 (1955).

[105] D.N. Kursanov, S.N. Parnes and T.A. Smolina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 512 (1952); D.N. Kursanov and Z.N. Parnes, ibid. 92, 341 (1953).

[106] V.N. Setkina and E.V. Bykov, Proc. Acad. Sci. USSR 92, 341 (1953).

[107] F.F. Lavrushin, D.N. Kursanov and V.N. Setkina, Proc. Acad. Sci. USSR, 97, 2 (1954).

[108] J.W. Otvos, D.P. Stevenson, C.D. Wagner and O. Beeck, J. Am. Chem. Soc. 73, 5741 (1951).

[109] D.P. Stevenson, C.D. Wagner, O. Beeck and J.W. Otvos, J. Am. Chem. Soc. 74, 3269 (1952).

[110] Ya.M. Varshavsky and A.I. Shatenshtein, Proc. Acad. Sci. USSR 95, 297 (1954); A.I. Shatenshtein and E.A. Izraelevich, J. Phys. Chem. 28, 3 (1954).

[111] V. Gold, B.W.V. Hawes and F.L. Tye, J. Chem. Soc. 2167 (1952).

[112] V. Gold and F.L. Tye, J. Chem. Soc. 2172 (1952).

[113] C. Reid, J. Am. Chem. Soc. 76, 3264 (1954).

[114] L.W. Picket, N. Muller and R.S. Mulliken, J. Chem. Phys. 21, 1400 (1953); J. Am. Chem. Soc. 76, 3600 (1954).

[115] T.L. Hum and S.C. Yu, J. Am. Chem. Soc. 76, 3367 (1954).

[116] D. Lipkin, D.E. Paul, I. Townsend and S.I. Weissmann, Science 117, 534 (1952).

[117] L. Schmerling, Ind. Eng. Chem. 45, 1447 (1953).

[118] L.V. Pisarzhevsky, Selected Works, Ukrainian Acad. Sci. Press (Kiev, 1936).

[119] G.N. Lewis, Valence and the Structure of Atoms and Molecules (1923).

[120] J. Steiglitz, J. Am. Chem. Soc. 44, 1293 (1922).

[121] R. Abegg, Z. anorg. Chem. 39, 330 (1904).

[122] P. Drude, Ann. Phys. 14, 722 (1904).

[123] L. Michaelis and M.P. Shubert, Chem. Rev. 22, 437 (1939); L. Michaelis, Theory of Oxidation–Reduction, in The Enzymes, Vol. II, part 1 (1951).

[124] A.N. Terenin, The Photochemistry of Dyes and Related Organic Compounds, Acad. Sci. USSR Press, Moscow – Leningrad (1947).

[125] Radiation Chemistry, Disc. Far. Soc. No. 12 (1952).

[126] J.N. Bronsted, Rec. trav. chim. 42, 718 (1923).

[127] T.M. Lowry, J. Soc. Chem. Ind. (L) 42, 43 (1923).

[128] G.N. Lewis, J. Frankl. Inst. 226, 292 (1938).

[129] W.F. Luder and S. Zuffanti, Electronic Theory of Acids and Bases (1946).

[130] M.I. Usanovich, J. Gen. Chem. 9, 182 (1939).

[131] A.A. Grinberg, Introduction to the Chemistry of Complex Compounds, 2nd Ed., Leningrad, State Chem. Press (1951).

[132] B. Flurshein, J. pract. Chem. 66, 321 (1902); 71, 497 (1905); J. Chem. Soc 1362 (1926)

[133] A.F. Holleman, Die direkte Einführung von Substituenten in den Benzolkern (Leipzig, 1910).

[134] F. Hinrich, Theorien der organischen Chemie, 5th ed., (1924).

[135] W. Hückel, Theoretical Principles of Organic Chemistry, Moscow, Foreign Lit. Press (1955).

[136] L.P. Hammett, Physical Organic Chemistry (New York, London, 1940).

[137] A.E. Remick, Electronic Interpretations in Organic Chemistry (New York, London, 1945).

[138] M.J.S. Dewar, Electronic Theory of Organic Chemistry (London, 1949).

[139] D. Vorländer and E. Siebert, Ber. 52, 283 (1919); D. Vorländer, Ber. 58, 1893 (1925).

[140] F.R. Goss, W. Haukart and C.K. Ingold, J. Chem. Soc. 250 (1927). C.K. Ingold and J.S. Wilson, ibid. 810 (1927).

[141] C.K. Ingold, F.R. Schaw and J. S. Wilson, J. Chem. Soc. 1280 (1928).

[142] J.W. Barker and W.G. Maffitt, J. Chem. Soc. 1722 (1930).

[143] M.S. Kharash, W.G. Brown and J. McNab, J. org. Chem. 2, 36 (1937), W.G. Brown, M.S. Kharash and W.R. Sprowes, J. org. Chem. 4, 442 (1939).

[144] O. Reitz, Handb. der Katalyse 2, 272 (1940).

[145] W.M. Latimer, Oxidation States of the Elements and their Potentials in Aqueous Solutions, Foreign Lit. Press (1954).

[146] A.N. Frumkin, V.S. Bagotsky, Z.A. Iofa and B.N. Kabanov, Kinetics of Electrode Processes, Moscow State Univ. (1952).

[147] A.I. Shatenshtein, Progr. Chem. 16, 548 (1947).

[148] A.I. Shatenshtein, Proc. Acad. Sci. USSR 70, 1029 (1950); J. Phys. Chem. 25, 1206 (1954).

[149] A.I. Shatenshtein, N.M. Dykhno, E.A. Izrailevich, L.N. Vasilyeva and M. Faivush, Proc. Acad. Sci. USSR, 79, 479 (1951).

[150] A.I. Shatenshtein, L.N. Vasilyeva, N.M. Dykhno and E.A. Izrailevich, Proc. Acad. Sci. USSR 85, 381 (1952).

[151] A.I. Shatenshtein, Progr. Chem. 21, 914 (1952).

[152] A.I. Shatenshtein, L.N. Vasilyeva and N.M. Dykhno, J. Phys. Chem. 28, 193 (1954).

[153] A.I. Shatenshtein, Symposium "Questions of Chemical Kinetics, Catalysis and Reactivity," Moscow, Acad. Sci. USSR Press, p. 691 (1955); see also [148].

[154] V.R. Kalinachenko, Ya.M. Varshavsky and A.I. Shatenshtein, Proc. Acad. Sci. USSR 91, 577 (1953).

[155] R.J. Gillespie, J. Chem. Soc. 2537 (1950).

[156] A. Klitz and A. Langseth, Z. phys. Chem. A176, 65 (1936).

[157] A.I. Shatenshtein and Yu.M. Varshavsky, Proc. Acad. Sci. USSR 85, 171 (1952).

[158] J. Nieuwland and R. Vogt, The Chemistry of Acetylene, A.C.S. Monograph No. 99 (1945).

[159] A.I. Rabinovich, V.A. Kargin and E.V. Fodiman, J. Phys. Chem. 2, 64 (1931).

[160] S.Z. Roginsky and A.I. Shalnikov, Koll.-Z. 43, 67 (1927).

[161] P.P. Shorygin, Investigations of the Metalloorganic Compounds of Sodium (1910).

[162] K.A. Kocheshkov and T.V. Talalaeva, Synthetic Methods in the Field of the Metalloorganic Compounds of Lithium, Sodium, Potassium, Rubidium and Cesium, Moscow, Acad. Sci. USSR Press (1949).

[163] K.A. Kocheshkov and T.V. Talalaeva, Proc. Acad. Sci. USSR 77, 621 (1951).

[164] A.I. Shatenshtein, Progr. Chem. 24, 377 (1955).

[165] W.K. McEven, J. Am. Chem. Soc. 58, 1124 (1936).

[166] G.P. Miklukhin, Progr. Chem. 17, 663 (1948).

[167] G.P. Miklukhin and A.F. Rekasheva, Symposium "Questions of Chemical Kinetics, Catalysis and Reactivity," Moscow, Acad. Sci. USSR Press, p. 24 (1955).

[168] A.I. Brodsky and I.G. Khaskin, Proc. Acad. Sci. USSR 74, 299 (1950).

[169] I.G. Khaskin, J. Gen. Chem. 23, 32 (1953).

[170] I.G. Khaskin, Proc. Acad. Sci. USSR 85, 129 (1952).

[171] M.M. Slutskaya, Zh.M. Shershever and A.I. Brodsky, J. Phys. Chem. 9, 417 (1937).

[172] P. Goldfinger and A. Lasareff, Comptes rend. 200, 1671 (1935).

[173] A.I. Brodsky and L.V. Sulima, Proc. Acad. Sci. USSR 74, 513 (1950).

[174] P.R. Girardot and R.W. Parry, J. Am. Chem. Soc. 73, 2368 (1951).

[175] R.E. Weston and J. Bigeleisen, J. Chem. Phys. 20, 1400 (1952); J. Hine and C.H. Thomas, J. Am. Chem. Soc. 75, 739 (1953).

[176] R.M. Adams, R.B. Bernstein and J.J. Katz, J. Chem. Phys. 23, 622 (1955).

[177] N.H. Kwart, L.P. Kuhn and E.L. Bannister, J. Am. Chem. Soc. 76, 5998 (1954).

[178] J.C. Jungers and K.F. Bonhoeffer, Z. phys. Chem. A177, 460 (1936).

[179] N.D. Sokolov, Problems of Kinetics and Catalysts 8, 141 (1955).

[180] E.J. Hart, S. Gordon and D.A. Hutchison, J. Am. Chem. Soc. 75, 6165 (1952).

[181] E.J. Hart, J. Phys. Chem. 56, 594 (1952).

[182] E.J. Hart, S. Gordon and D.A. Hutchison, J. Am. Chem. Soc. 74, 5548 (1952).

[183] A.I. Brodsky, Progr. Chem. 6, 152 (1937).

[184] L.A. Webster, M.H. Wahl and H.C. Urey, J. Chem. Phys. 3, 411 (1935).

[185] M. Cohn and H.C. Urey, J. Am. Chem. Soc. 60, 679 (1938).

[186] J.B.M. Herbert and I. Lauder, Trans. Far. Soc. 34, 432 (1938); M. Senkus and W.G. Brown, J. org. Chem. 2, 569 (1938).

[187] N.F. Hall and O.R. Alexander, J. Am. Chem. Soc. 62, 3455 (1940); E.R.S. Winter, M. Careten and H.V. Briscal, J. Chem. Soc. 131 (1940).

[188] A.I. Brodsky and A.V. Sulima, Proc. Acad. Sci. USSR 92, 589 (1953); A.I. Brodsky and E.I. Dontsova, Proc. Acad. Sci. Ukrainian SSR 3 (1939); 39 (1940); A.I. Brodsky and N.A. Vysotskaya, Proc. Acad. Sci. USSR 101, 869 (1955).

[189] H. Dodgen and H. Taube, J. Am. Chem. Soc. 71, 2501 (1949).

[190] M. Haissinsky and K. Daudel, Bull. Soc. Chim. France 552 (1947)

[191] A.I. Brodsky, Symposium "Questions of Chemical Kinetics, Catalysis and Reactivity," Acad. Sci. USSR Press, Moscow, p. 18 (1955).

[192] L. Szilard and T. Chalmers, Nature 134, 462 (1934).

[193] E. Amaldi, E. Fermi, F. Rasetti and E. Segre, Nuovo Cimento 50, 442 (1934).

[194] N.E. Brezhneva and S.Z. Roginsky, Progr. Chem. 7, 1538 (1938).

[195] R.N. Rubinshtein, Diploma Paper, Leningrad Polytech. Inst. (1937).

[196] J. Barnes, W. Burgus and J. Miskel, Radioactivity Applied to Chemistry, Foreign Lit. Press (1954).

[197] N.E. Brezhneva, S.Z. Roginsky and A.I. Shilinsky, J. Phys. Chem. 8, 849 (1936).

[198] A. Murin and Yu. Taush, Proc. Acad. Sci. USSR 80, 579 (1951).

[199] Ya.A. Fialkov and Yu.P. Nazarenko, Bull. Acad. Sci. USSR, Div. Chem. Sci. 590 (1950).

[200] A.R. Olson, C.W. Porter, F.A. Long and Halford, J. Am. Chem. Soc. 58, 12 (1936).

[201] K.B. Zaborenko, M.B. Neiman and V.I. Samsonova, Proc. Acad. Sci. USSR 64, 541 (1949).

[202] A.S. Polesitsky, Proc. Acad. Sci. USSR 24, No. 6 (1939).

[203] A.A. Grinberg and F.M. Filippov, Proc. Acad. Sci. USSR 23, 918 (1939); 31, 453 (1941); A.A. Grinberg and L.E. Nikolskaya, J. Appl. Chem. 22, 242 (1949).

[204] Ya.A. Fialkov and Yu.P. Nazarenko, Proc. Acad. Sci. USSR 69, 201 (1949); 73, 727 (1950); Proc. Acad. Sci. Ukrainian SSR 417 (1950).

[205] Ya.A. Fialkov and Yu.P. Nazarenko, Ukrain. Chem. J. 19, 356 (1953).

[206] Ya.A. Fialkov, Complex Compounds of Aluminum Halides and Polyhalides, Acad. Sci. Ukrainian SSR (Kiev, 1947).

[207] Ya.A. Fialkov, Progr. Chem. 15, 485 (1946).

[208] Ya.A. Fialkov and A.A. Kuzmenko, J. Gen. Chem. 6, 2624 (1936).

[209] D.E. Hull, C.H. Shiflet and S.C. Lind, J. Am. Chem. Soc. 58, 535 (1936).

[210] F. Juliusburger, B. Topley and J. Weiss, J. Chem. Phys. 3, 437 (1935).

[211] R.L. Richardson and S.W. Benson, J. Am. Chem. Soc. 73, 5096 (1951).

[212] F. Fairbrother, J. Chem. Soc. 847 (1936); 503 (1937); 293 (1941).

[213] Tables of Chemical Kinetics, Homogeneous Reactions, Nat. Bureau of Standards (1951) (Table 302477)

[214] G.A. Elliot and S. Sugden, J. Chem. Soc. 1837 (1939).

[215] R.M. Noyes, R.G. Dickinson, and V. Schomaker, J. Am. Chem. Soc. 67, 1319 (1945).

[216] A. Werner, Lehrbuch der Stereochemie (1904).

[217] A. Uspensky, supplement to P. Walden's book "Stereochemistry, Past and Present," Leningrad, Theoret. Chem. Press (1926).

[218] G. Wittig, Stereochemistry, Moscow, State Tech. Press (1934).

[219] N. Meer and M. Polanyi, Z. phys. Chem. 19B, 164 (1932).

[220] F. Bergmann, M. Polanyi and A.L. Szabo, Z. phys. Chem. 20B, 161 (1933).

[221] A.L. Szabo, Dissertation, Berlin (1933); E. Bergmann, M. Polanyi and A.L. Szabo, Trans. Far. Soc. 32, 843 (1936).

[222] E.D. Hughes, I. Juliusburger, A.D. Scott, B. Topley and J. Weiss, J. Chem. Soc. 1173 (1936); 1525 (1936).

[223] W.A. Cowdrey, E.D. Hughes, T.P. Nevell and C.L. Wilson, J. Chem. Soc. 209 (1938).

[224] V.B. Miller, M.B. Neiman and Yu.M. Shapovalov, Proc. Acad. Sci. USSR 75, 419 (1950); 85, 1289 (1952).

[225] S.Z. Roginsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 601 (1940).

[226] M.B. Neiman, Yu.M. Shapovalov and V.B. Miller, J. Phys. Chem. 28, 1243 (1954).

[227] M.B. Neiman, V.B. Miller and Yu.M. Shapovalov, Symposium, "Questions of Chemical Kinetics, Catalysis and Reactivity," Moscow, Acad. Sci. USSR Press, p. 722 (1955).

[228] M.B. Neiman, B.A. Kuznetsov and Yu.M. Shapovalov, Proc. Acad. Sci. USSR 92, 611 (1953).

[229] H. McKay, J. Am. Chem. Soc. 65, 702 (1943).

[230] H. Seelig and D. Hull, J. Am. Chem. Soc. 64, 940 (1942).

[231] Yu.M. Shapovalov, Dissertation, Inst. Phys. Chem., Acad. Sci. USSR (1953).

[232] R. Halford, J. Am. Chem. Soc. 62, 3233 (1940).

[233] L. Le Roux and S. Sugden, J. Chem. Soc. 1279 (1939).

[234] A.A. Grinberg, Progr. Chem. 9, 771 (1940).

[235] H. Taube, Chem. Rev. 50, 69 (1952).

[236] A.A. Grinberg, L.E. Nikolskaya and G.A. Shagisultanova, Symposium, "Questions of Chemical Kinetics, Catalysis and Reactivity," Acad. Sci. USSR Press, p. 633 (1955); Proc. Acad. Sci. USSR 101, 1059 (1955).

[237] N.K. Pshenitsyn and S.I. Ginzburg, Ann. Sector Platinum and other Noble Metals 24, 100 (1949).

[238] A. Adamson, J. Welker and W.B. Wright, J. Am. Chem. Soc. 73, 4786 (1951).

[239] A.W. Adamson, J. Am. Chem. Soc. 73, 5710 (1950).

[240] A.W. Adamson and R.G. Wilkins, J. Am. Chem. Soc. 76, 3379 (1954).

[241] A.A. Grinberg and L.E. Nikolskaya, J. Appl. Chem. 24, 893 (1951).

[242] I.I. Chernyaev, Bull. Inst. Platinum, Acad. Sci. USSR 4, 244 (1926); 5, 118 (1927).

[243] F.A. Long, J. Am. Chem. Soc. 63, 1353 (1941).

[244] G.M. Harris, J. Chem. Phys. 18, 764 (1950).

CHAPTER IV.

ISOTOPE EFFECTS IN CHEMICAL KINETICS

§1. Special Features of the Problem

The theory of kinetic isotope effects has a common spectroscopic, statistical, and thermodynamic basis with the theory of isotope effects in chemical equilibria, considered in Chaper I. However, there is a difference in principle between calculations of thermodynamic and kinetic effects. Any equilibrium involving isotopes, like any other equilibrium, can in principle be calculated to any desired degree of accuracy if the external conditions and certain characteristic properties of the initial and final substances are known. These may be thermochemical functions (F and S) or data on the structures, masses, or energy levels of the molecules, but in all the methods the calculations are based on quantities which may be determined directly or calculated from experimentally determined material constants, irrespective of the chemical process. The mechanism and rate of the latter do not affect, directly or indirectly, the value of the equilibrium constant or the thermodynamic isotopic corrections.

As was shown in Chapter I, in most cases, for the calculation of thermodynamic isotope effects, it is sufficient to know, in addition to the stoichiometric equation and the reaction temperature, either the zero point energies of the initial and final substances, or the fundamental vibration frequencies which are directly related to them.

The theory of absolute chemical reaction rates is far more complex. The stoichiometric equation for the reaction does not play any significant role in rate calculations, while the composition and physical properties of the original and final substances do not give sufficient data for the calculation. The rate depends on the actual reaction mechanism, the presence and concentrations of positive or negative catalysts, the conditions and the nature of the determining stage. The rate theory lacks the definiteness which is so characteristic of the equilibrium theory.

This may be illustrated by the following example. In the equilibrium theory the magnitude of isotope effects falls rapidly with increasing isotope mass, and these effects are negligibly small for the heavy elements. In most instances, but not always, this is also true of kinetic isotope effects. There are exceptions. For example, the rates of photochemical reactions induced by resonance radiation may differ considerably for different isotopes of heavy elements. The work of Billings, Hitchcock and Zelrkoff [1], who studied the photochemical oxidation of mercury vapor by water vapor, is instructive in this respect. The reaction vessel was illuminated from outside by a quartz arc using mercury strongly enriched with the Hg^{198} isotope. Under the action of resonance radiation from such an arc with a wavelength of 2536.5 A, which differs for Hg^{198} by about 0.01 A from the average wavelength of the same radiation for the stable isotope group Hg^{199}, Hg^{200}, Hg^{201}, Hg^{202} and Hg^{204} [2], the mercury atoms in the apparatus undergo electronic excitation. As was noted in Chapter III, the probability of photon capture becomes greater as the excitation level of the absorbing atom approaches the value of the photon energy (resonance). Resonance radiation of Hg^{198} is absorbed most strongly by atoms of the 198 isotope. As a result, the rate of the photochemical reaction according to the scheme

$$\left.\begin{array}{c} Hg + h\nu \rightarrow Hg^* \\ Hg^* + H_2O \rightarrow HgH + OH \\ HgH + OH \rightarrow HgO + H_2 \\ \hline Hg^* + H_2O \rightarrow HgO + H_2 \end{array}\right\} \qquad (1)$$

is higher for Hg^{198} than for the other isotopes.

Mass spectrum investigations of the contents of different isotopes in the original metallic mercury and the mercury oxide formed showed a 1.5-fold enrichment with the Hg^{198} isotope. Consequently, $k_{Hg^{198}} : k_{Hg} = 1.5$, i.e., the rate constant for the 198 isotope is 50% higher than for the natural mixture of isotopes, nearly 90% of which consists of the heavier isotopes from 199 to 204. These differences are greater by 2-3 orders of magnitude than the differences given by the statistical theory of equilibria (see Chapter I) and rates (see below, §2) for thermal reactions of mercury atoms according to the equation

$$\left.\begin{array}{l} Hg + O_2 \rightarrow 2HgO; \\ Hg + H_2O \rightarrow HgO + H_2 \end{array}\right\} \tag{2}$$

In fact no enrichment in excess of the theoretically expected value was observed in any of the thermal reactions of mercury. This example shows the great influence of the method of activation of the original substances on the magnitude of chemical isotope effects.

In the above example, because of the peculiar inner mechanism the isotopic effects for heavy atoms were very high. The opposite effect – anomalously small differences of isotopic reaction rates – may be expected in reactions of the oxidation-reduction type and in instances in which tunnel transfer of electrons is the rate-determining process.

The reaction conditions are very important. The kinetic isotope effect for a particular reaction at a given temperature may differ, under extreme kinetic and diffusion conditions, not only in magnitude but in sign. Appreciable changes in the magnitude of isotope effects may also accompany transitions from pure to mixed conditions, or from control by internal diffusion to control by external diffusion [3].

However, even after the conditions and the stages of the chemical process have been determined for given conditions, difficulties remain owing to the indefinite nature of the labile intermediate forms in the process. The great majority of chemical reactions consist of several or many simple stages. In particular conditions some of these stages may occur practically reversibly. For these, isotopic equilibria can be calculated with adequate accuracy from the equations in Chapter I. Some stages may be practically irreversible but, in the modern view, each simple irreversible stage includes the intermediate reversible formation of a short-lived intermediate collision complex, or a complex resulting from intramolecular regrouping, generally known as an intermediate complex [4]. The rates of the elementary steps of a complex reaction and the total rate of a simple reaction may, in principle, be represented by multiplying the concentrations of the activated complexes $c^{\#}$ by their reciprocal average lives and the conversion factor κ. The latter is the ratio of the probabilities of conversion of the intermediate complex in the forward and reverse directions. The concentration $c^{\#}$ and the concentrations of the initial substances are connected by the equation

$$c^{\#} = K^{\#} f(c_1; c_2; \ldots), \tag{3}$$

where $K^{\#}$ is the constant for the equilibrium of the activated complex with the initial substances. Hence

$$w = \frac{1}{\tau} K^{\#} \cdot \varkappa f(c_1; c_2; \ldots) = kf(c_1; c_2; \ldots), \tag{3a}$$

where τ is the average life of the intermediate complex, and $\frac{1}{\tau}$ is the conversion frequency for $\kappa = 1$.

The form of the function f is determined from kinetic data or is based on a definity hypothesis concerning the number and type of particles constituting the intermediate complex. Both the value of κ and the value of $K^{\#}$ depend on the detailed structure of the intermediate complex. However, there are no direct methods for determination of zero-point energies, fundamental frequencies, and rotational sums of the intermediate complexes when these consist of groups of molecules at the instant of chemically effective collision. There are also no direct methods for determining the mass and nature of the particles moving along the transition coordinate (see below). Because of this, calculations of the equilibrium constants $K^{\#}$ by statistical methods are generally uncertain. Insufficient information on the properties of the intermediate complexes also makes statistical calculations of isotopic corrections for the rate constants of simple molecular chemical reactions uncertain.

For complex reactions additional difficulties arise because of possible errors in selecting the stage which determines the rate of the process, and because the isotopic corrections for the rates of different stages may be additive in some cases and partially compensating in others. Because of the difficulty of definite and reliable calculations, a priori calculations are at present impossible in the more complex cases, and it becomes necessary to make direct determinations of the required quantities or to estimate them by analogy with previously investigated reactions of a similar type. For the same reason, many theoretical investigations consist of searches for intermediate complex models which can explain the experimentally observed isotopic corrections. Since a general solution is not obtainable from the theory, experimental data on the magnitudes of kinetic isotope effects become of independent importance as material for the derivation of relationships between the isotopic corrections and the characteristics of the system.

Kinetic isotope effects are small for all elements except hydrogen, and for reliable determinations the errors in determinations of the rate constants should be considerably less than the effects in question. It is therefore undesirable to determine isotope effects by comparisons of the results of independent experiments performed with systems of different isotopic compositions. It is difficult in such cases to attain the required exact agreement between the experimental conditions. In particular, quite often a temperature difference of only a few hundredths of a degree may produce variations of k which exceed the differences due to isotopic composition. The demands with regard to purity of the substances used, agreement between the solution acidities, etc., are also very rigorous. In order to avoid these difficulties in making a comparison, differences between the isotopic composition of the initial substances and of the reaction products are taken as a basis. In this case both the external and the chemical conditions for the two compared reactions are identical throughout the experiment. However, in such investigations confusion is also possible as the result of redistribution of isotopes in side reactions. Thus, it is a very difficult task to obtain clear experimental results on the influence of isotopic composition on chemical reaction rates. It is not surprising that quite often the data of different authors on the kinetic isotope effects for the same reaction, carried out apparently under the same conditions, are sharply contradictory. However, in cases in which the experimental difficulties have been surmounted, comparisons of experimental and calculated isotope effects provide very valuable information on the inner mechanisms of the reactions, and primarily on the structure and properties of the intermediate complexes in the rate-determining stages.

These possibilities have so far been used quite inadequately, but we may assume that in the near future exact determinations of kinetic isotope effects will become one of the principal methods for the study of reaction mechanisms, especially as the experimental difficulties formerly encountered in determinations of small isotope effects have been eliminated owing to the use of differential methods, by which the relative contents of kinetically the most important isotopes can be determined to an accuracy of 0.1%, and sometimes down to hundredths of one per cent.

§2. Statistical Theory of Isotope Kinetic Corrections

Modern methods for calculation of isotope kinetic corrections are based on the use of the equations of statistical thermodynamics for isotopic equilibria, discussed in Chapter I, and the kinetic theory of the intermediate state, often known also as the theory of absolute reaction rates. The basic fundamental idea of the latter was formulated as long ago as 1915 by Marcelin [5], but it was only on the basis of wave mechanics that Eyring, Polanyi, and Evans [4, 6] succeeded in making this theory quantitative. During the 20 years of existence of the statistical theory of chemical reaction rates its physical basis has been repeatedly verified, and can now be regarded as generally accepted [7]. M.I. Temkin [8] and Kimball [9] have shown that it is fully applicable to heterogeneous gaseous catalysis and to chemisorption.

Details are to be found in the well known monograph by S. Glasstone, K. Laidler and H. Eyring [4] and in various publications of recent years [10-12]; we will note here that, despite the success achieved [13], the weakness of this theory is the inaccuracy of the quantum-mechanical methods for calculation of activation energies from the bond energies of the reacting molecules. Only in cases when the activation energy is known experimentally or does not appear in the final calculations can the intermediate state (complex) theory act as a sound basis for comparison with experimental data.

Calculations of isotope effects from the statistical theory are based on comparisons of the expressions for the rate constants of the same reaction for molecules of different isotopic composition. These expressions are derived from formulas analogous to Equation (2) in the preceding section, and in this case the defects of the theory of absolute reaction rates do not significantly affect the accuracy of the result

Let us consider a homogeneous gaseous reaction between molecules A, B, C, etc., leading, through an intermediate complex [ABC]..., to a new system X. Suppose that the initial system contains molecules A_1 and A_2, identical in all but molecular weight, which differs because of a different isotopic composition of one of the elements.* Then, by Equation (3), the rate constants k_1 and k_2 for analogous reactions, proceeding through the intermediate complexes $[A_1BC]$ and $[A_2BC]$, may be written as

and

$$\left.\begin{aligned} k_1 &= K_1^{\#} \varkappa_1 \tau_1^{-1} \\ k_2 &= K_2^{\#} \varkappa_2 \tau_2^{-1} \end{aligned}\right\}. \tag{4}$$

In Equations (4), $K_1^{\#}$ and $K_2^{\#}$ are equilibrium constants which, with the aid of Equations (33) and (34) of Chapter I, can be represented in terms of concentrations of the initial substances and intermediate complexes, or of the corresponding statistical sums

$$\begin{aligned} K_1^{\#} &= \frac{c_1^{\#}}{c_{A_1} c_B \cdots} = \frac{Z_1^{\#}}{Z_{A_1} Z_B \cdots}, \\ K_2^{\#} &= \frac{c_2^{\#}}{c_{A_2} c_B \cdots} = \frac{Z_2^{\#}}{Z_{A_2} Z_B \cdots} \end{aligned} \tag{5}$$

Quantum-mechanical analysis [4] leads to the following expression for the reciprocal life of the intermediate complex

$$\tau^{-1} = \frac{\bar{v}}{\delta}, \tag{6}$$

where $\bar{v}$ is the average rate for the passage of the activated complex over the energy barrier

$$\bar{v} = \left(\frac{kT}{2\pi\bar{m}}\right)^{1/2}, \tag{7}$$

while δ is the width of the latter at the top (Fig. 57). In Equation (7) k is the Boltzmann constant and $\bar{m}$ is the so-called effective mass of the intermediate complex along the decomposition coordinate.

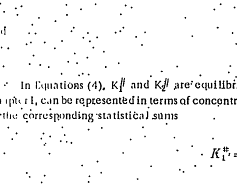


Fig. 57. Diagram of activation barrier with indication of vibrational levels. Variation of potential energy during the reaction is shown [4].

It was shown by Slater [14] in an extensive investigation of considerable importance for the theory of kinetic isotope effects that the effective mass can, in certain cases, coincide with the reduced mass

$$\bar{m} \approx \mu = \frac{mm'}{m + m'}, \tag{8}$$

of the two atoms between which the chemical bond is broken in the decomposition of the intermediate complex. In other cases it is a fairly complex function of the masses of the radicals or molecules forming the intermediate complex. Substituting $\bar{v}$ from (7) into Equation (6), we have

$$\tau^{-1} = \left(\frac{kT}{2\pi\bar{m}}\right)^{1/2} \frac{1}{\delta}. \tag{9}$$

In this form no correction is made for the possibility of tunnel leakage through the barrier (see Chapter III), which may be predominant for electrons and appreciable for hydrogen isotopes at low temperatures. According to Wigner [15], to apply the tunnel correction $1/\tau$ must be multiplied by the factor $[1 - u_L^2/24]$, where

---

*But not because of association or dissociation.

$$u_L = hc\omega_L / kT. \tag{10}$$

In this expression ω_L is the frequency of the stretching vibrations along the transition coordinate. The full expression for τ^{-1} has the form

$$\tau^{-1} = \tau_{\text{class}}^{-1}\left[1 - \frac{1}{24}\left(\frac{hc\omega_L}{kT}\right)^2\right]. \tag{11}$$

Using Equations (4), (5) and (9), we obtain expanded expressions for k_1 and k_2 without the tunnel factor

$$\left.\begin{aligned} &\text{a)}\quad k_1 = \varkappa_1 \frac{Z_1^{\#}}{Z_{A_1} Z_B}\left(\frac{kT}{2\pi\bar{m}_1}\right)^{1/2} \frac{1}{\delta_1}; \\ &\text{b)}\quad k_2 = \varkappa_2 \frac{Z_2^{\#}}{Z_{A_2} Z_B}\left(\frac{kT}{2\pi\bar{m}_2}\right)^{1/2} \frac{1}{\delta_2}. \end{aligned}\right\} \tag{12}$$

Since the molecules B, C, etc., and their appropriate factors in Equations (5) and (12) are identical, changes of isotopic composition have a very weak effect on the geometry of the molecules and their force functions, and therefore it is natural to assume that $\delta_1 = \delta_2$. On this assumption, and in view of the presence of common factors in Equations (12, a and b) we obtain the very simple Equation (13) for the ratio of rate constants for molecules differing in isotopic composition. This expression was apparently first derived by Bigeleisen [16]

$$k_1 : k_2 = \left(\frac{\varkappa_1}{\varkappa_2}\right)\left(\frac{Z_1^{\#}}{Z_2^{\#}}\right)\left(\frac{Z_{A_2}}{Z_{A_1}}\right)\left(\frac{\bar{m}_2}{\bar{m}_1}\right)^{1/2} \tag{13}$$

Let us examine separately each of the four fractional factors in the right-hand side of Equation (13). The first of them is the least clear. In calculations of absolute reaction rates κ is often taken to be $1/2$, while in the isotope effect theory it is assumed that $\frac{\kappa_1}{\kappa_2} = 1$. However, as will be seen later, the validity of this assumption is debatable.* The second and third fractions are the already familiar ratios of the statistical sums Z^*/Z for analogous molecules of different isotopic composition, written without isolation of the exponential factor with zero-point energies in explicit form. Exact and approximate expressions for the ratio Z^*/Z were given in Chapter I (in Tables 10 and 14 of Chapter I this is Q_2^*/Q_1). A good approximation for the isotopes of all elements except hydrogen is provided by Equation (100) of Chapter I, which includes the function G, proposed by Bigeleisen and Mayer [17] (see §9, Chapter I) for the free energy. Using the notation of Chapter I, we may replace the second and third factors in Equation (13) by the fraction $\frac{f_A}{f^{\#}} \cdot \frac{\sigma_2^{\#}\sigma_1}{\sigma_1^{\#}\sigma_2}$, where the separation function f_A refers to A molecules, and $f^{\#}$ to the intermediate complexes.

$$\frac{k_1}{k_2} = \left(\frac{\varkappa_1}{\varkappa_2}\right)\frac{f_A}{f^{\#}}\frac{\sigma_2^{\#}}{\sigma_1^{\#}}\frac{\sigma_1}{\sigma_2}\left(\frac{\bar{m}_2}{\bar{m}_1}\right)^{1/2}. \tag{14}$$

By the condition assumed in Chapter I, the subscripts 2 apply to the lighter, and subscripts 1 to the heavier molecules. By Equation (98a and b) of Chapter I the functions f are expressed in terms of G and the reduced energies of fundamental vibrations $u_i = \hbar\omega_i c/kT$ as follows

$$f = \prod_i \left[1 + G(u_i)\,\Delta u_i\right]. \tag{15}$$

If the terms $G(u_i)\,\Delta u_i$ are small, the product $\prod_i$ in Equation (15) may be with good approximation replaced by the sum

---

*κ_1/κ_2 may be greater or less than 1, but cannot greatly differ from it.

$$f = 1 + \sum_i \left[\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1}\right]\Delta u_i. \qquad (16)$$

Because of this, and also of the existence of 3n – 6 vibrational degrees of freedom in a molecule containing n atoms, the ratio k_1/k_2 becomes

$$\frac{k_1}{k_2} = \frac{\sigma_2^{\#}\sigma_1}{\sigma_1^{\#}\sigma_2}\left(\frac{\varkappa_1}{\varkappa_2}\right)\left(\frac{\overline{m_2}}{\overline{m_1}}\right)\left[1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n'-6} G(u_i^{\#})\Delta u_i^{\#}\right]. \qquad (17)$$

In view of the smallness of all the correction terms for tunnel leakage, it is sufficient to multiply the right-hand side of Equation (17) by the expression $\left(1 + \frac{u^2_{l\,(2)} - u^2_{l\,(1)}}{24}\right)$

$$\frac{k_1}{k_2} = \frac{\sigma_2^{\#}\sigma_1}{\sigma_1^{\#}\sigma_2}\left(\frac{\varkappa_1}{\varkappa_2}\right)\left(\frac{\overline{m_2}}{\overline{m_1}}\right)\times$$
$$\times\left[1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n'-6} G(u_i^{\#})\Delta u_i^{\#}\right]\left(1 + \frac{u^2_{l\,(2)} - u^2_{l\,(1)}}{24}\right). \qquad (17a)$$

We shall now give an approximate expression for the difference of the activation energies for analogous reactions of two isotopic molecules. By definition

$$E = kT^2\frac{d\ln k}{dT}, \qquad (18)$$

and hence

$$\frac{E_1 - E_2}{kT^2} = \frac{d\ln(k_1/k_2)}{dT}, \qquad (18a)$$

and after substitution of the value of k_1/k_2 from Equation (17)

$$\frac{E_1 - E_2}{kT^2} = \frac{d\ln\left(\frac{\varkappa_1}{\varkappa_2}\right)}{dT} + \frac{u^2_{l\,(2)} - u^2_{l\,(1)}}{12T} + \sum_i^{3n-6}\left[\frac{e^{u_i}(u_i - 1) + 1}{(e^{u_i} - 1)^2} - \frac{1}{2}\right]\frac{\Delta u_i}{T} -$$
$$- \sum_i^{3n'-6}\left[\frac{e^{u_i^{\#}}(u_i^{\#} - 1) + 1}{(e^{u_i^{\#}} - 1)^2} - \frac{1}{2}\right]\frac{\Delta u_i^{\#}}{T}. \qquad (19)$$

In the derivation of Equation (19) the function G was written in explicit form, and the constant factors containing σ and m vanished. It is probable that the ratio $\varkappa_1/\varkappa_2$ may, without introducing any large error, be regarded as independent of the temperature. In that case even the first term of Equation (19) becomes zero.

In general the influence of tunnel leakage through the barrier is slight, and therefore the second term can also be rejected. The resulting inaccuracy is less for higher atomic weights and temperatures. We are therefore left with the formula

$$E_1 - E_2 = kT\sum_i^{3n-6}\left[\frac{e^{u_i}(u_i - 1) + 1}{(e^{u_i} - 1)^2} - \frac{1}{2}\right]\Delta u_i -$$
$$- kT\sum_i^{3n'-6}\left[\frac{e^{u_i^{\#}}(u_i^{\#} - 1) + 1}{(e^{u_i^{\#}} - 1)^2} - \frac{1}{2}\right]\Delta u_i^{\#}. \qquad (19a)$$

To complete the analysis of Equation (17), let us briefly consider the ratio of two effective masses. In cases in which motion of the system along the transition coordinate corresponds to the rupture of a definite bond as the result of an increase in the vibrational energy of stretching of this bond, each value of $\overline{m}$ is equal to the corresponding reduced mass μ, and therefore

$$\left(\frac{\overline{m_2}}{\overline{m_1}}\right)^{1/2} = \left(\frac{\mu_2}{\mu_1}\right)^{1/2} = \left[\frac{m_2(m + m_1)}{m_1(m + m_2)}\right]^{1/2}, \qquad (20)$$

where m is the mass of the atom which is the same for the two isotopic molecules, in the broken bond, and m_2 and m_1 are the masses of the isotopic atoms. For example, in the rupture, in the intermediate complex of $N^{14} - C^{12}$ and $N^{14} - C^{13}$ bonds, m = 14, m_2 = 12 and m_1 = 13 hydrogen units. In Eyring's theory $\overline{m}$ was often taken to be identical with the mass of the whole intermediate complex, and subsequently the vibration of the intermediate complex at one of the bonds was replaced by translational motion. In this case, instead of 3n – 6, 3n – 7 factors remained in the vibrational sum for the intermediate complex, and a translational factor appeared for the transition coordinate.

$$f^{\#}_{tr\,(1)} = \frac{(2\pi mkT)^{1/2}}{h}\delta. \qquad (21)$$

Introduction of this factor and subsequent rearrangement converts Equation (12) into Equation (22), which does not contain $\overline{m}$ in explicit form

$$k_l = \frac{kT}{h}\frac{Z^{\#}}{Z_A Z_B}. \qquad (22)$$

With this transformation, the ratio k_1/k_2 no longer contains $\varkappa_1/\varkappa_2$ and $(\overline{m_2}/\overline{m_1})^{1/2}$, but the ratio $(M_2/M_1)^{1/2}$ remains in implicit form as the equivalent of $(\overline{m_2}/\overline{m_1})^{1/2}$, where M_2 and M_1 are the masses of the lighter and heavier intermediate complexes.

With the original Equation (22), Equation (17) becomes

$$\frac{k_1}{k_2} = \Pi\sigma_l\left[1 + \sum_i^{3n-6} G(u_i\Delta u_i) - \sum_i^{3n'-6} G(u_i^{\#})\Delta u_i^{\#}\right]. \qquad (17a)$$

It is evident that the method of calculating $(\overline{m_2}/\overline{m_1})^{1/2}$ used by Bigeleisen [16, 18] differs significantly from the method used by Eyring [4]. This may lead to appreciable differences in the calculated values of the isotope effects.

The equations given above form the basis for calculations of isotopic kinetic effects for all elements except hydrogen. For the latter, at low temperatures, the discontinuity of the rotational statistical sums must be taken into account, and therefore the more complex equations given in Chapter I must be used. The Bigeleisen equations contain the factors $\varkappa_1/\varkappa_2$ and $(\overline{m_2}/\overline{m_1})^{1/2}$ which can neither be directly measured nor calculated exactly. This also applies to the tunnel correction, which depends on the form of the activation barrier, for which no determination methods exist at present; finally, in the sum $\sum_i^{3n-6} G(u_i^{\#})\Delta\mu_i^{\#}$ some of the terms are not sufficiently well defined. Therefore absolute calculations of isotopic kinetic corrections are of an approximate nature for most reactions. This makes reaction types for which these uncertainties diminish or vanish of all the greater theoretical interest.

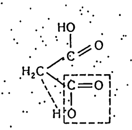
§ 3. Intramolecular Isotope Effects

The calculation of isotope effects is greatly simplified if rates of analogous processes in groups in the same molecule, differing only in isotopic composition, are compared. An example of such reactions is the decomposition of di-, tri- or polycarboxylic organic acids, which has been studied with particular detail for the decomposition of malonic acid, $CH_2(COOH)_2$ and its derivatives. When malonic acid is heated above its melting point it is quantitatively decomposed into acetic acid and carbon dioxide

$$CH_2(COOH)_2 \rightarrow CH_3COOH + CO_2. \qquad (23)$$

The same reaction occurs at lower temperatures in certain solvents, for example, in dilute hydrochloric acid at 100°C.

The decomposition may be schematically represented as the rupture of one C–C bond; accompanied by hydrogen migration



Because natural carbon contains both C^{12} and C^{13}, every sample contains molecules with only the main carbon isotope, molecules containing a mixture of C^{12} and C^{13}, and finally, molecules with C^{13} only. Because of the low content of C^{13} (its occurrence is 1.1%, or 90 times less than the occurrence of C^{12}), the participation of $H_2C^{13}\begin{array}{l} C^{13}OOH \\ C^{12}OOH \end{array}$, $H_2C^{12}\begin{array}{l} C^{13}OOH \\ C^{13}OOH \end{array}$ and $H_2C^{13}\begin{array}{l} C^{13}OOH \\ C^{13}OOH \end{array}$ molecules containing more than one C^{13} atom in the reaction may be neglected.*

4 processes will occur in pyrolysis, simultaneously and independently:

$$\begin{array}{l}
1)\ H_2C^{12}-(C^{12}OOH)_2 \xrightarrow{2k_1} C^{12}H_3C^{12}OOH + C^{12}O_2; \\
2)\ H_2C^{12}\begin{array}{l} C^{12}OOH \\ C^{13}OOH \end{array} \xrightarrow{k_2} C^{12}H_3C^{12}OOH + C^{13}O_2; \\
3)\ H_2C^{12}\begin{array}{l} C^{12}OOH \\ C^{13}OOH \end{array} \xrightarrow{k_3} C^{12}H_3C^{13}OOH + C^{12}O_2; \\
4)\ H_2C^{13}(C^{12}OOH)_2 \xrightarrow{2k_4} C^{13}H_3C^{12}OOH + C^{12}O_2.
\end{array} \qquad (24)$$

For malonic acid with the natural content of C^{13}, it may occur with equal probability, to the accuracy of the very small isotope effect, in any of the three positions, and therefore there should be twice as many molecules with C^{13} in the carboxyl as with C^{13} in the methylene group. By using preparations strongly enriched with C^{13}, or malonic acid tagged with C^{14}, it is possible to regulate the position of the tagged atom and to obtain preparations in which practically all the C^{14} (or C^{13}) is in the methylene or in the carboxyl groups.

In the decomposition of tagged malonic acid carbon dioxide is formed by all four reactions simultaneously. To make the results comparable, with a single reaction referred to one carboxyl group, it is necessary to double the constants for the first and fourth reactions, which is equivalent to taking the symmetry numbers into account. Of the four reactions, only the second produces tagged carbon dioxide, and the other three give acetic acid and $C^{12}O_2$. If all the k's, referred to one carboxyl group, are equal, the reaction should not be accompanied by a change in the fractional C^{13} content. The magnitude of the isotopic corrections is determined by the difference between k_2 and the other constants. There are two main types of bond rupture in the reactions represented by Equations (24): in Reactions 1) and 3) the $C^{12}-C^{12}$ bond is broken, and in Reactions 2) and 4), the $C^{12}-C^{13}$ bond (once with the C^{13} in the carboxyl group, and once with the C^{13} in the methylene group). The experimental results show that the isotope differences in the bonds which are not directly involved in the reaction either have no effect at all on k, or have a weaker effect; therefore it may be assumed that $k_1 = k_3$.

Reactions 2) and 3) represent two variations of the decomposition of the same type of molecule, the only difference being the isotopic composition of the breaking bond. Differences of isotopic composition which appear

---

* With the usual sensitivity of the method it is also possible to neglect the presence of molecules containing radioactive carbon C^{14}, the occurrence of which in organic molecules in equilibrium with the atmosphere is negligible.

in reactions of this type are termed intramolecular isotope effects. In principle, an intramolecular isotope effect should also be found in the comparison of

$$H_2C^{13}\begin{array}{l} C^{12}OOH \\ C^{12}OOH \end{array} \text{ and } H_2C^{13}\begin{array}{l} C^{12}OOH \\ C^{13}OOH \end{array}$$

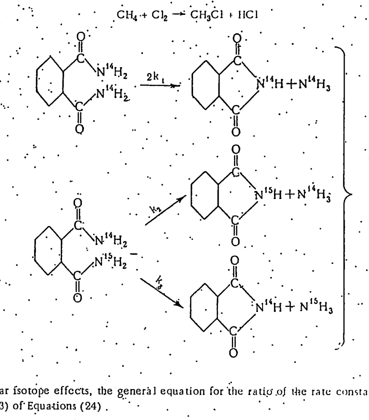
More generally, we may speak of intramolecular isotope effects in all cases when a molecule R_nP (where R and P are atoms or radicals) reacts with a substance A, forming $R_{n-1}P$ and AR_1, all R being chemically identical, but one (or several) differs isotopically from the others. This term was first proposed in 1951 by Lindsay, Bourns and Thode [19]. Experimental studies of isotopic corrections for reactions of this type began 2-3 years earlier, in view of the simplicity of the theory of such effects.

As a second example of the intramolecular effect, we shall consider the thermal deamination of phthalamide tagged with N^{15}. Three isotopic reactions are represented by Equations (26).

The separation of nitrogen isotopes in this reaction was studied by Stacey, Lindsay and Bourns [20], and a detailed calculation of the isotope effect was made by Bigeleisen [21].

In principle, an internal isotope effect should be expected also in reactions such as

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \qquad (25)$$



(26)

For intramolecular isotope effects, the general equation for the ratio of the rate constants of the two compared reactions 2) and 3) of Equations (24)

$$\frac{k_2}{k_3} = \frac{\sigma_2\sigma_3^{\#}}{\sigma_3\sigma_2^{\#}}\frac{\varkappa_2}{\varkappa_3}\left(\frac{\overline{m}_3}{\overline{m}_2}\right)^{1/2}\left[1 + \sum_{i}^{3n-6} G(u_i)\,\Delta u_i - \sum_{i}^{3n'-6} G(u_i^{\#})\,\Delta u_i^{\#}\right] \qquad (17)$$

is very much simplified. Because the original molecules coincide not only in chemical, but also in isotopic composition and in the mechanism, the fraction

$$\frac{\sigma_2\sigma_3^{\#}}{\sigma_3\sigma_2^{\#}} = 1. \qquad (27)$$

Each term of the first sum in the square brackets represents the product of G for a definite i-th vibration and the difference u_i for the same vibration in molecules of different isotopic composition.

Since the original molecules are isotopically identical [22, 23]

$$\sum_{i}^{3n-6} G(u_i)\,\Delta u_i = 0. \tag{28}$$

The intermediate complexes for reactions 2) and 3) are completely analogous structurally (they are isotopic isomers), and therefore it is natural to assume that the second sum, after the minus sign in the square brackets, is practically equal to 0

$$\sum_{i}^{3n'-6} G(u_i^{\#})\,\Delta u_i^{\#} \approx 0 \tag{28a}$$

As a result, the factor which represents the ratio of the zero-point energies in the expression for k_2/k_3 becomes 1, and the equation assumes the extremely simple form

$$\frac{k_2}{k_3} = \frac{\varkappa_2}{\varkappa_3}\left(\frac{\overline{m}_3}{\overline{m}_2}\right)^{1/2} \tag{29}$$

The remarkable feature of Equation (29) is the absence of any quantities which depend on the temperature in its right-hand side. Therefore the ratio of the rates of two analogous reactions and the intramolecular isotope effect should not vary with the temperature. It may be noted that as a measure of the kinetic isotope effect the ratio $\alpha = k_2/k_3$ is taken in some cases, and $\delta = k_2/k_3 - 1$ in others. We shall use both coefficients in discussing the magnitude of intramolecular isotope effects. The fraction $\varkappa_2/\varkappa_3$ is often taken equal to unity. Then

$$k_2/k_3 \approx (\overline{m}_3/\overline{m}_2)^{1/2} \tag{29a}$$

We shall now evaluate the fraction $(\overline{m_3}/\overline{m_2})^{1/2}$, and hence k_2/k_3 in Equation (29a) for several examples, assuming, according to Slater [14], that $\overline{m} = \mu$.

Isotopes of carbon

It follows from the detailed balancing principle [24] for elementary chemical processes that the kinetic isotope effects should be equal for the forward and reverse reactions. Therefore it is not significant for their magnitude whether particular chemical bonds are broken or formed. At the determining stage only the masses of the atoms linked by such bonds are important. This evident proposition has been worked out in detail and substantiated by Bigeleisen [21].

Let us take as our basis the $C^{12}-C^{12}$ bond, and calculate the magnitude of the kinetic isotope effect, with rupture (or formation) of this bond competing with the $C^{12}-C^{13}$, $C^{12}-C^{14}$ and $C^{12}-C^{11}$ bonds. Table 74 gives the corresponding values of μ and $\mu^{1/2}$.

By using these values for finding the fractions $(\mu_i/\mu_i')^{1/2}$, it is easy to find the calculated values of

$$\alpha = \frac{k_i}{k_i'} = \left(\frac{\mu_i'}{\mu_i}\right)^{1/2}.$$

Table 75 gives these values for different bonds: C − C; C − H; C − N and C − Cl.

This table shows that even after exclusion of the temperature-dependent terms which represent the influence of differences in the zero-point energies of molecules of different isotopic compositions, isotopic kinetic effects δ may remain, measurable in tenths of one per cent for carbon–hydrogen bonds.

Since the calculated value depends only on the ratio of the masses, it may be stated without performing a separate calculation, that intramolecular isotopic corrections for reactions in which the determining steps are formation or rupture of bonds between hydrogen and oxygen or nitrogen will have similar values. For bonds between carbon atoms, between carbon and nitrogen or oxygen, and between oxygen and nitrogen, the intramolecular isotope corrections δ, due to the mechanism in question, lie in the range of 1.5 to 4.0%; and, finally, as the example of the C − Cl bond shows, bonds between chlorine and carbon, nitrogen, or oxygen, and between phosphorus or sulfur and carbon, nitrogen, or oxygen, the intramolecular isotope corrections calculated from Equation (29a) are tenths of one per cent. Since the above theory is of an approximate nature, the data in the tables are given only to a small number of figures and great accuracy is not claimed for the calculated values of k_i and k_i'. It must be remembered that the above calculation is not valid for reactions of the type under consideration if electron transfer becomes rate-determining or if the rate of the process is affected by the equilibrium concentrations of intermediate substances which have higher stabilities than intermediate complexes.

TABLE 74

Values of μ and $\mu^{1/2}$ for C − C Bonds of Different Isotopic Compositions

Bond	μ in hydrogen units	$\mu^{1/2}$	Bond	μ, in hydrogen units	$\mu^{1/2}$
I. C−C bond					
Homoisotopic			Heteroisotopic		
$C^{11}-C^{11}$	5.5	2.35	$C^{12}-C^{11}$	5.74	2.40
$C^{12}-C^{12}$	6.0	2.45	$C^{12}-C^{13}$	6.24	2.50
$C^{13}-C^{13}$	6.5	2.55	$C^{12}-C^{14}$	6.46	2.54
$C^{14}-C^{14}$	7.0	2.65	$C^{13}-C^{11}$	5.90	2.43
			$C^{13}-C^{14}$	6.74	2.59
			$C^{14}-C^{11}$	6.14	2.47
II. Other $C^{12}-X$ bonds					
$C^{12}-H$	0.923	0.960	$C^{12}-O^{16}$	6.86	2.62
$C^{12}-D$	1.71	1.32	$C^{12}-O^{18}$	7.2	2.69
$C^{12}-T$	2.4	1.55	$C^{12}-Cl^{35}$	8.91	2.98
$C^{12}-N^{14}$	6.46	2.54	$C^{12}-Cl^{37}$	9.06	3.01
$C^{12}-N^{15}$	6.66	2.58			

TABLE 75

Intramolecular Kinetic Isotope Effects α for Certain Bond Pairs

Bond	α	Bond	α
I. C — C		III. C — H	
12—12/12—13	1.02	12—1/12—2	1.37
12—12/12—14	1.04	12—1/12—3	1.62
12—11/12—12	1.02	12—2/12—3	1.18
II. C — N		IV. C — Cl	
12—14/12—15	1.015	12—35/12—37	1.007

§ 4. Experimental Data on the Magnitude of Intramolecular Kinetic Isotope Effects

The literature contains extensive experimental data on kinetic isotope effects. Before the theory of these effects had been developed, most of the investigations were performed in relation to methods for separation and enrichment of isotopes, mainly with hydrogen isotopes. Thermal, photochemical, and electrochemical reactions in the liquid and gaseous phases were studied from this angle, the main attention being devoted to reactions with large isotope effects, such as the formation of methane by the action of water on aluminum carbide or the electrolysis of water. On the whole, it may be said that as a rule kinetic isotope effects are of the same order of magnitude as the thermodynamic effects. They reach appreciable magnitudes only for hydrogen. In particular, ordinary water reacts with aluminum carbide according to the equation

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

at 0°C, 20 times as rapidly as heavy water

$$Al_4C_3 + 12D_2O \rightarrow 4Al(OD)_3 + 3CD_4$$

Tritium water reacts still more slowly. These large effects mainly depend on differences of zero-point energies both of the original molecules and of the intermediate complexes.

Theoretical analysis of this case is more difficult than for intramolecular isotope effects, and therefore a considerable proportion of recent quantitative investigations has been devoted to reactions of this type, with correlation of the experimental results obtained by new and improved methods, with the theory presented above.

Table 76 contains Bigeleisen's data [34], with minor additions, on experimental and calculated values of intramolecular isotope effects for 8 reactions.

The fourth column shows the possible error for each experimental value of α. The estimate seems to be excessively optimistic.

Examination of the data in Table 76 shows the extent to which the Bigeleisen–Eyring–Slater theory is applicable to the description of experimental results and to the prediction of new effects.

There is no doubt that, despite the far-reaching approximations made in the derivation of the fundamental equation, the theoretically calculated corrections are in all cases close to the experimentally observed values. In some instances the agreement is complete or very good (Reactions 1, 3, 8, 9). In some cases the deviations are appreciable and of a systematic character (Reactions 2, 4, 5, 6 and 7). In all cases the observed deviations are of the same sign – the experimental isotope effects, expressed in terms of δ, are greater than the theoretical, often being about double the latter. It is perhaps no accident that of the five instances of appreciable deviations between calculated and experimental values, four refer to molecules tagged with C^{14}. The effects of temperature on the intramolecular isotope effect have not been studied systematically enough, but, to judge from Table 76, instead of the complete independence of k_2/k_3 of the temperature predicted by the theory, there is a gradual decrease in the magnitude of the effect with increase of temperature. The greatest deviation between theory and experiment is found in the influence of different carbon isotopes. By the theory, $\delta = (k_2/k_3 - 1)$ for C^{14} should be 1.9 times the value for C^{13}; in fact, the increase may be very much greater, for example, for Reaction 1, 4.5 times. On the whole, the isotope corrections δ for $C^{12} - C^{14}$ are more than double the theoretical.

It seems likely that many usual intermolecular reactions are intramolecular in their determining stages, but other mechanisms are also possible, and therefore Equation (29a) may be used not only for comparison of theory with experiment, but to determine whether a reaction is to be classified as intramolecular.

§ 5. Kinetic Effects in Reactions of Other Types in Solutions

Until recently, experimental methods required for reliable determinations of small kinetic isotope effects were available only to a few laboratories. The theoretical interpretation of the influence of changes of isotopic composition on the rates of chemical reactions was also not sufficiently clear. Therefore, while scattered individual observations have been abundant, systematic data on intramolecular kinetic effects are available for only a few reactions in solutions. However, despite the paucity of experimental data, some relationships can be established. For example, the nature of the directly broken or newly formed bonds in which the atoms of the com-

TABLE 76

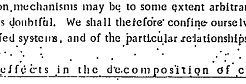
Intramolecular Isotope Effects

Reaction	Compared intramolecular bonds	T, °C	k_2/k_3 exp.	Literature	k_2/k_3 theor.	Notes
1 $CH_2(COOH)_2 \rightarrow CO_2 + CH_3COOH$	$C^{12}—C^{12}/C^{12}—C^{13}$	138	1.020±0.001	[25]		
		138	1.021±0.001	19	1.020	
		138	1.026±0.001	26		
2. $CH_2(COOH)_2 \rightarrow CO_2 + CH_3COOH$	$C^{12}—C^{12}/C^{12}—C^{14}$	150	1.12±0.03	27		
		153	1.06±0.02	28	1.038	
		138	1.088–1.10	26		
3. $BrCH(COOH)_2 \rightarrow CO_2 + BrCH_2COOH$	$C^{12}—C^{12}/C^{12}—C^{14}$	115	1.41±0.08	27	1.038	
4 $R_1CH(COOH)_2 \rightarrow CO_2 + R_1CH_2COOH$ R_1 — α-naphthyl	$C^{12}—C^{12}/C^{12}—C^{14}$	163	1.076±0.002	29	1.038	Liquid
		72.8	1.098±0.012	29		In dioxane in presence of 1 N HCl
		87.5	1.095±0.008	29		
5 $R_2CH(COOH)_2 \rightarrow CO_2 + R_2CH_2COOH$ R_2 - phenyl	$C^{12}—C^{12}/C^{12}—C^{14}$	163	1.088±0.018	29	1.038	Liquid
		62.8	1.132±0.017			In dioxane in presence of 1 N HCl
6 $(COOH)_2 \xrightarrow{\text{conc.}H_2SO_4} CO + CO_2 + H_2O$	$C^{12}—C^{12}/C^{12}—C^{13}$	80.1	1.0325±0.001	30	1.020	Solution in 99.4% H_2SO_4
		103	1.027±0.0022			
		100	1.032	31		Recalculated.
7 $(COOH)_2 \xrightarrow{\text{conc.}H_2SO_4} CO + CO_2 + H_2O$	$C^{12}—C^{12}/C^{12}—C^{13}$	80.1	1.067±0.0035	30	1.038	Solution in 99.4% H_2SO_4
		103	1.055±0.003	30	1.038	
8 $NH_4NO_2 \rightarrow N_2 + 2H_2O$	$N^{14}—O^{16}/N^{15}—O^{16}$	220	1.023±0.003	22	1.026	
9 Phthalamide → phthalimide + NH_3	$C^{12}—N^{14}/C^{12}—N^{15}$	136	1.016±0.001	20	1.016	See Equation (26), p. 237.

pared isotopes participate is decisive for intermolecular reactions also, and the magnitude of the effect is approximately the same if the determining stage includes bond rupture or formation. In addition to reactions giving quite definite isotope effects, reactions are found which proceed at practically identical rates with different isotopic compositions. Zero or extremely small isotope effects are characteristic for reactions of certain types, for example: reactions of electrolytes with rate-determining electron transfer; reactions in which the determining stage is hydrogen migration, with differences in isotopic composition of carbon, nitrogen, or other elements, etc. In view of the paucity of the experimental data the generality of these relationships is not certain, especially as the interpretations of the reaction mechanisms may be to some extent arbitrary. Moreover, the reliability of some of the experimental data is doubtful. We shall therefore confine ourselves to the presentation of the experimental results for the best-studied systems, and of the particular relationships which follow from these results.

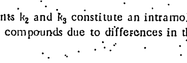
Intermolecular kinetic effects in the decomposition of carboxylic acids

Even in the decomposition of dicarboxylic acids, discussed in §3, there are intramolecular as well as intermolecular isotope effects. For example, in the decomposition of oxalic acid, changes of the isotopic composition of CO_2, CO, and $(COOH)_2$ caused by branching



$$\begin{array}{l}\overset{*}{C}OOH \\ | \quad (H_2SO_4) \\ COOH\end{array} \begin{array}{l}\xrightarrow{k_2} \overset{*}{C}O + H_2O + CO_2 \\ \xrightarrow{k_3} \overset{*}{C}O_2 + H_2O + CO\end{array} \tag{30}$$

and differences between the rate constants k_2 and k_3 constitute an intramolecular isotope effect, while changes in the isotopic composition of the same compounds due to differences in the rate constants of Reactions (30) and (30a), involving untagged oxalic acid



$$\begin{array}{l}COOH \\ | \\ COOH\end{array} \xrightarrow{H_2SO_4} CO_2 + CO + H_2O \tag{30a}$$

constitute an intermolecular isotope effect.

The intermolecular nature of the isotopic effects in the decomposition of monocarboxylic acids of the type

$$\left.\begin{array}{l}RCOOH \rightarrow RH + CO_2, \\ R\overset{*}{C}OOH \rightarrow RH + \overset{*}{C}O_2\end{array}\right\}$$

is still more evident. Intermolecular isotope effects in the decomposition of carboxylic acids have been studied by many authors [31; 32], and analyzed theoretically by Pitzer [33], Bigeleisen [34, 25], and others. Bigeleisen's detailed examination of the problem was based on the same approximate initial Equations (14) and (15), and the fairly crude assumption was made that all the corrections may be referred to one single bond (the C – C bond in the carboxylic acids) with variable isotopic composition. Initially the ratio of the effective masses ($\overline{m_i}$) was taken as the ratio of the masses of $C^{12}O_2$ and $C^{13}O_2$, or of $C^{12}O_2$ and $C^{14}O_2$, respectively. Later, in agreement with Slater, $\left(\frac{\overline{m_2}}{\overline{m_1}}\right)^{1/2}$ was taken as equal to $\left(\frac{\mu_{C^{12}-C^{12}}}{\mu_{C^{12}-C^{14}}}\right)^{1/2}$, where μ represents the reduced masses. In some cases corrections were also introduced for strengthening of bonds not ruptured directly according to the reaction scheme, or allowances were made for hidden thermodynamic effects resulting from the preliminary formation of labile equilibrium forms – tautomers, ortho-forms, etc.

Neither the Bigeleisen and Mayer functions $G(u_i)$ and $G(u_i^{\#})$, nor the differences $G(u_i)\,\Delta u_i$ and $G(u_i^{\#})\,\Delta u_i^{\#}$ in the formulas (17) and (17a) for intermolecular isotope effects can be completely calculated from spectroscopically determined vibration frequencies for given bonds, as $\omega_i^{\#}$ for the intermediate complex is unknown. Values of u_i of the original stable molecules, and the corresponding Δu_i and $G(u_i)$ may be based on the average value given above, of $\omega_{C^{12}-C^{12}} \approx 900\ cm^{-1}$. This value ω is close to the average frequency of the stretching vibration of the $C^{12} - C^{12}$ bond found from Raman spectra. This value of ω may, with the aid of the equations given in §9, Chapter I, be easily used to calculate $\omega_{C^{12}-C^{13}}$ and $\omega_{C^{12}-C^{14}}$.

The interesting calculations made by Eyring and Cagle [35] are simpler and approximately as accurate. In these calculations it is also assumed that one or two bonds play a predominant role in the origin of the isotope kinetic effect, but it is assumed that the activation barriers for analogous reactions of molecules differing in isotopic composition are identical in form and height. Because of this assumption, in the complete expression for $\alpha = k_1/k_3$, the main factor which determines the value of α is the fraction $\frac{Z_{vibr}}{Z^*_{vibr}}$ for a definite bond, and Eyring expresses α in the form

$$\alpha = \frac{k_1}{k_3}\,\frac{Z_{vibr}}{Z^*_{vibr}} \approx \frac{2\sin h\,(hc\omega_i/2kT)}{2\sin h\,(hc\omega_i^*/2kT)} = \frac{\sin h\,(hc\omega_i/2kT)}{\sin h\,(hc\omega_i^*/2kT)} \tag{31}$$

In this approximate formula sinh is the hyperbolic sine [36], which, by definition, is the sum of the infinite series

$$\sin h\,(x) = \sum \frac{x^{2n+1}}{(2n+1)!} = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \tag{32}$$

or the sum of two exponential functions

$$\sin h\,(x) = \frac{e^x - e^{-x}}{2} \tag{32a}$$

with an approximate value, for high values of x

$$\sin h\,(x) \approx \frac{e^x}{2} \tag{32b}$$

and for low values of x

$$\sin h\,(x) \approx x. \tag{32c}$$

$$\left.\begin{array}{l}\text{In the present case } x = hc\omega_i/2kT \\ \text{and correspondingly, } x^* = hc\omega_i^*/2kT.\end{array}\right\} \tag{33}$$

The fractions in the right-hand sides of Equations (33) are the reduced zero-point energies or $\frac{u_i}{2}$. Z and ω_i refer to a definite broken bond for one isotope, and Z^* and ω_i^* to the same bond for another isotope. An advantage of Equation (31) is the absence of quantities explicitly dependent on the properties of the intermediate complex.

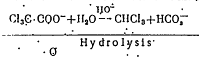
The Eyring–Cagle equation is a special case of the more general Bigeleisen equation, valid for certain limiting conditions.

Table 77 gives the values of intermolecular kinetic isotope effects determined for certain reactions in solutions, and calculated theoretically.

Table 77 shows that the statistical theory correctly predicts the nature of the influence of isotope mass and temperature on the rate also for intermolecular isotope effects in solutions. For three of the five reactions given the theoretical values of α are also close to the experimental values. Since the calculation is absolute in character and involves no experimental data apart from bond frequencies and masses, this agreement between theory and experiment must be regarded as convincing proof of the fundamental principles of the theory. The same method and the same equations are applicable also if the rate-determining step is accompanied by formation and not rupture of bonds. Of the reactions given in Table 77, the first two occur in strongly acid solutions, the third and fourth in alkaline solutions, and the fifth in weakly acid solution. The first four reactions are examples of homogeneous acid–base catalysis, while the last is an example of biological catalysis. It is perhaps no accident that in this case the discrepancy between theory and experiment is particularly large.

TABLE 77

Intermolecular Isotope Effects for Certain Reactions in Solutions, after Bigeleisen [34], with Additions

	Reaction	Isotopes compared	T, °C	k/αk* exp.	k/σk* theoret.	Literature
	Decarboxylation					
1	$CH_2(COOH)_2 \xrightarrow{H_2SO_4} CO_2 + CH_3COOH$	C^{12}/C^{13}	138	1.037+0,002	1.035	[34]
			137	1.034		
			149	1.041		
			173	1.034	1.031	
			196	1.036		
2		C^{12}/C^{13}	61.2	1.037+0.003	—	[34]
			60.0	1.038+0.001	1.041	
			92.0	1.032+0.001	1.038	
		C^{12}/C^{14}	60.0	1.101+0.007	1.078	
3	$Cl_3C \cdot COO^- + H_2O \xrightarrow{HO^-} CHCl_3 + HCO_3^-$	C^{12}/C^{13}	70.4	1.0338+0,007	1.040	[34]
	Hydrolysis					
4	$C_6H_5\overset{O}{\overset{\Vert}{C}}-O-C_2H_5 + OH^- \rightarrow C_6H_5COOH + C_2H_5O^-$	C^{13}/C^{14}	25	1.16	1.15	[37]
			25	1.076	1.15	
5	$CO(NH_2)_2 + H_2O \xrightarrow{Urease} CO_2 + 2NH_3$	C^{12}/C^{13}	30	1.01	1.045	[38]
		C^{12}/C^{14}	30	1.03	1.088	

§ 6 Isotope Effects in the Kinetics of Hydrogen Reactions

According to the general theoretical principles and the data in Table 77, kinetic isotope effects are particularly large for the reactions of hydrogen and its compounds. An interesting comparison between theory and experimental data was made in this connection by Eyring and Cagle [35], with the aid of Equation (31). The most detailed calculation was made for the electrolysis of ordinary and semideuterated water, on the basis of the Erdey–Gruz and Volmer mechanism [39]. In accordance with this theory, the authors represent the primary reaction step at the electrodes as follows:

$$\left.\begin{array}{l} 1)\ HOH + Me \rightarrow HO \ldots H \ldots Me \rightarrow HO + HMe; \\ 2)\ DOH + Me \rightarrow DO \ldots H \ldots Me \rightarrow DO + HMe; \\ 3)\ HOD + Me \rightarrow HO \ldots D \ldots Me \rightarrow HO + DMe \end{array}\right\} \qquad (34)$$

k_1 should differ little from k_2; $k_1 \approx k_2$. Therefore $\frac{d[H]}{d[D]} = \frac{2k_1(H_2O) + k_2(DHO)}{k_3(DHO)}$ becomes

$$\frac{d[H]}{d[D]} = \frac{k_1[H]}{k_3[D]}, \qquad (35)$$

where [H] and [D] are the concentrations of hydrogen and deuterium atoms in the water molecules. From this, values of α are easily found.

Integration of Equation (35) after separation of the variables gives

$$\frac{d\ln[H]}{d\ln[D]} = \alpha = \frac{k_1}{k_3} \approx \frac{\sinh(hc\omega_{OH}/2kT)}{\sinh(hc\omega_{OD}/2kT)}, \qquad (36)$$

where ω_{OH} and ω_{OD} are the fundamental vibrations of the O–H and O–D bonds in water. At [illegible] °C, assuming $\omega_{OH} = 3652$ cm^{-1} and $\omega_{OD} = 2666$ cm^{-1}, Eyring and Cagle [35] found $\alpha = 10.8$. For Ag, Ni, Pt, Au, Cu, Pb the experimentally found values of α lie between 6 and 7. Because of the simplifications used, which are very rough in view of this very peculiar and heterogeneous process, the calculated values of α represent the upper limit of possible values. It is seen that for the reaction in question, α for which is 6-7 times as high as for the processes considered earlier, while δ is about 2 orders of magnitude higher, the theory also gives the right order of magnitude. It follows from this theory that α should diminish with increasing temperature, tending to the ratio of the effective masses which appears in Equation (29a) for intramolecular isotope effects (Fig. 58).

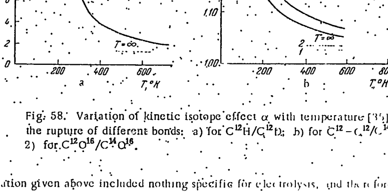


Fig. 58. Variation of kinetic isotope effect α with temperature [35] for the rupture of different bonds: a) for $C^{12}H/C^{12}D$; b) for $C^{12}-C^{12}/C^{14}-C^{12}$, 2) for $C^{12}O^{16}/C^{14}O^{16}$.

The calculation given above included nothing specific for electrolysis, and therefore it may also be applied to the production of CH_4 or CD_4 respectively by the action of H_2O and D_2O on Al_4C_3. If the specific characteristics of the system are taken into account, it is possible to explain the unusually high value of α found experimentally for this reaction, which reaches 20 at room temperature. Satisfactory agreement with Equation (31) is also obtained for the isotope effect in the dehydration of formic acid in sulfuric acid solutions. The assumption that in this case the rate-determining step is rupture of the C–O bond at values of $\omega_{C^{12}-O^{16}} = 1093$ cm^{-1} and $\omega_{C^{14}-O^{16}} = 1047$ cm^{-1} leads to $\delta = 12.8\%$ at 0°C and $\delta = 11.5\%$ at 25°C. Ropp, Weinberger and Neville [40] obtained the experimental values of $\delta = 11.1\%$ at 0°C and 8.6% at 25°C.

§ 7. Maximum Theoretically Possible Values of Kinetic Isotope Effects

The above examples demonstrate the validity of the statistical theory at high values of α and δ and the applicability of Equation (31) in theoretical analysis.

Since in calculations of kinetic isotope effects the main source of differences between the rate constants lies in differences between the vibrational stretching frequencies of definite bonds, and in the corresponding differences of the zero-point energies, it is easy to calculate the values of the maximum possible isotope effects for different isotope pairs in absence of hidden thermodynamic effects summated with purely kinetic effects. This has been done in Table 78, taken from Bigeleisen's paper [41]. All the values of α refer to one bond. In more accurate calculations it is necessary to take into account additional quantities which diminish α, and the possibility of superposed hidden thermodynamic effects.

The calculations in Table 78 were made for the extreme model, on the assumption that the atoms of the corresponding isotopes in the intermediate complex move as free atoms. Despite this, the calculated values of α are of the right order of magnitude. It should be stressed that the estimated values of α still differ appreciably from unity for the elements of the second and even the third period of the periodic system. With a sufficiently

TABLE 78

Estimate of Maximum Possible Kinetic Isotope Effects α at 25°C, after Bigeleisen

Normal isotope	Tagged isotope	α_{max} per bond	Normal isotope	Tagged isotope	α_{max} per bond
H	D	18	O^{16}	O^{18}	1.19
H	T	60	F^{19}	F^{18}	1.25
Li^{6}	Li^{7}	1.1	Na^{23}	Na^{22}	1.03
Be^{9}	Be^{7}	1.15	Na^{23}	Na^{24}	1.03
Be^{9}	Be^{10}	1.08	Mg^{24}	Mg^{27}	1.08
B^{10}	B^{11}	1.3	P^{31}	P^{32}	1.02
C^{12}	C^{13}	1.25	S^{32}	S^{35}	1.05
C^{12}	C^{14}	1.5	Cl_{nat}	Cl^{36}	1.03
N^{14}	N^{15}	1.14	Cl_{nat}	Cl^{38}	1.14
N^{14}	N^{13}	1.14	Ca^{40}	Ca^{45}	1.08
N^{14}	N^{16}	1.25	J^{127}	J^{131}	1.02

fine technique the differences might be detected even for iodine I^{127} and I^{131}.

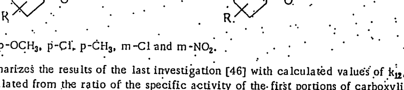
It is clear that for all the elements starting from Li including carbon, nitrogen, oxygen, sulfur and phosphorus, the maximum values of the isotope kinetic effects given in Table 78 cannot interfere with the use of the corresponding stable and radioactive isotopes as tagged atoms. There can only be the question of introducing corrections, which in practice are usually less than the tabulated values. The situation is different with the isotopes of hydrogen, for which the maximum values are so large that they can distort the true picture; therefore care is necessary in this case. Fortunately, the value of α for hydrogen falls rapidly with increase of temperature, and in most cases of interest in kinetics and catalysis the use of deuterium and tritium as tagged atoms is quite legitimate.

Further comparative data on isotope effects for the ordinary elements may be found in Ropp's paper [42].

§8. Effect of Substituents on the Activation Energies and Entropies of Reactions

An interesting series of publications has recently appeared on the magnitude of isotope effects for certain reactions of carbonyl compounds. These investigations were started by Attree and Stevens [43]. Valuable additions were made by Brown and Holland [44], while Ropp and Raaen [45, 46], conferred a systematic character on them.

The experimental work was performed with acids and ketones tagged with C^{14} in the carbonyl group. The reaction investigated most fully was the saponification of R-substituted ethyl benzoates according to the scheme



(37)

The R radicals were $p\text{-}OCH_3$, p-Cl, $p\text{-}CH_3$, m-Cl and $m\text{-}NO_2$.

Table 79 summarizes the results of the last investigation [46] with calculated values of $k_{12}/k_{14} = \alpha$. This coefficient was calculated from the ratio of the specific activity of the first portions of carboxylic acid formed, for example $\rho_{3\%}$, to the specific activity of the same product at 100% conversion. Strictly speaking (see Chapter V),

$$k_{12}/k_{14} = \rho_{0\%}/\rho_{100\%}. \qquad (38)$$

TABLE 79

Kinetic Isotope Effects in Saponification of Esters Containing C^{14} in the α-Position to the Benzene Ring [46]

Ester	Temperature, °C	Solvent	Ester concentration, M	Average k_{12}/k_{14}
Ethyl benzoate	0	90% ethanol	0.32	1.090
	25	90% ethanol	0.32	0.077
	78.5	90% ethanol	0.32	1.065
	25	50% acetone	0.32	1.078
	25	90% ethanol	1.60	1.080
Ethyl p-methoxybenzoate	25	90% ethanol	0.32	1.092
	25	56% acetone	0.32	1.091
Ethyl p-chlorobenzoate	25	90% ethanol	0.32	1.081
Ethyl p-methylbenzoate	25	90% ethanol	0.32	1.078
Ethyl m-chlorobenzoate	25	90% ethanol	0.32	1.072
Ethyl m-nitrobenzoate	25	90% ethanol	0.32	1.067
tert.-butyl benzoate	25	56% acetone	0.32	1.065

Consequently, the nearer to zero-percentage saponification the first sample is taken, the more accurate are the results. By commencing the isotope analysis at 3% conversion (sometimes 6%) the authors introduce an error of the order of 0.2% of the value measured; which has little effect on the results, which are in good agreement. From the data of Table 79 several interesting relationships can be deduced.

1. A 5-fold variation of ester concentration has only a very slight effect on the value of α. The difference hardly exceeds the experimental error.

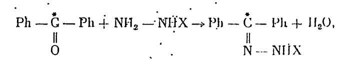
2. Replacement of 90% ethanol by 56% acetone also has no effect, so that the magnitude of the effect is insensitive to the external medium.

3. α (and, accordingly, δ) decreases with increasing temperature. Assuming that α depends on the temperature according to the Arrhenius law, it is possible to determine the approximate activation energy difference $\Delta E = E_{14} - E_{12}$. The calculation gives about 46 cal/mole.

These three relationships are in agreement with the statistical theory of isotope effects.

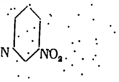
4. Of the three substituents introduced into the aromatic nucleus in the para-position, two – OCH_3 and Cl increase α, while the methyl group has no appreciable influence. Both the substituents in the meta-position, Cl and NO_2, decrease the isotope effect. Replacement of ethyl by tertiary butyl has the same effect. These effects produced by substituents can be regarded as a peculiar manifestation of the laws of electrophilic substitution in the aromatic nucleus, discussed in §14, Chapter III.

Brown and Holland [44] were the first to study the magnitude of the isotope effect in the formation of hydrazones from ketones and substituted hydrazines $XNH - NH_2$, for the reaction of benzophenone and dinitrophenylhydrazine



$$Ph-\underset{\underset{O}{\|}}{\overset{*}{C}}-Ph + NH_2-NHX \rightarrow Ph-\underset{\underset{N-NHX}{\|}}{\overset{*}{C}}-Ph + H_2O, \qquad (39)$$

where X is 2,4-dinitrophenyl



In this case formation of the C = N bond is the determining step. Analysis of the kinetics of parallel reactions of A and Å with the same reagents B and C, of the first order with respect to A and any order with respect to B and C leads to the very simple Equation (42a), similar to Equation (36). We denote the concentrations of A and Å, B and C, remaining at time t, by (a – x); (a* – x*); (b – x – x*) and (c – x – x*), and then:

$$\left.\begin{aligned} \text{a)}\ \frac{dx^*}{dt} &= k^*(a^*-x^*)(b-x-x^*)^n(c-x-x^*)^m \\ \text{b)}\ \frac{dx}{dt} &= k(a-x)(b-x-x^*)^n(c-x-x^*)^m \end{aligned}\right\} \tag{40}$$

Division of (40, b) by (40, a) gives

$$\frac{dx/dt}{dx^*/dt} = \frac{k(a-x)(b-x-x^*)^n(c-x-x^*)^m}{k^*(a^*-x^*)(b-x-x^*)^n(c-x-x^*)^m} = \frac{k(a-x)}{k^*(a^*-x^*)} \tag{41}$$

Cancellation of like factors and rearrangement gives the equation

$$k^*\frac{dx}{a-x} = k\frac{dx^*}{a^*-x^*} \tag{42}$$

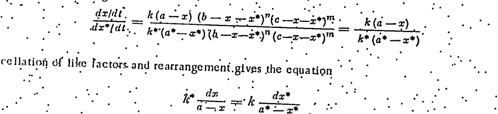
and, after integration:

$$\frac{k}{k^*} = \ln\frac{a}{a-x} \Big/ \ln\frac{a}{a^*-x^*} \tag{42a}$$

This equation, or an analogous equation in which a* and x* were replaced by ρ_{a^*} and ρ_{x^*}, was used to calculate $\alpha = k/k^*$; the following value for this ratio was found at 27.8°C

$$\alpha = \frac{(k_{\text{benzo ph-C}^{12}})}{(k_{\text{benzo ph-C}^{14}})} = 1.099 \pm 0.011, \text{ or } \delta = 0.099 \pm 0.01$$

In agreement with theory, the order of magnitude of δ for the reaction proceeding with formation of C = N bonds was the same as for reactions involving rupture of bonds between carbon and nitrogen or oxygen. Ropp and Raaen carried out a similar investigation for the reaction of dinitrophenylhydrazine with acetophenone, and studied the influence of the same parameters as in the case of hydrolysis of ethyl benzoates.

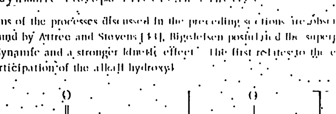


(43)

The R groups used were p-OCH$_3$ and m-NO$_2$; α was calculated from $\rho_{30\%}/\rho_{100\%}$. The reaction was performed in concentrated sulfuric acid solutions. The experimental relationships were found to be the same as for the saponification of esters. Thus, as the temperature was changed from –75 to +78°C; α fell from 1.101 to 1.043, which corresponds to ΔE = 49 cal/mole. Here also p-OCH$_3$ increased and m-NO$_2$ decreased the value of α. At 25°C without substituents, α = 1.057, with p-OCH$_3$ it was 1.072, and with m-NO$_2$, 1.042. The opposite influences of para- and meta-substituents is typical for aromatic compounds. The authors of this paper consider that their results are in agreement with Hammett's rule [48]. If this is so, ortho-substitution should change α in the same direction as para-substitution.

§9. Hidden Thermodynamic Isotope Effects in Kinetics

The inner mechanisms of the processes discussed in the preceding sections are obscure. To explain the earlier high values of α found by Attree and Stevens [44], Bigeleisen postulated the superposition of two isotope effects: a weaker thermodynamic and a stronger kinetic effect. The first relates to the equilibrium of transition into the enol form with participation of the alkali hydroxyl

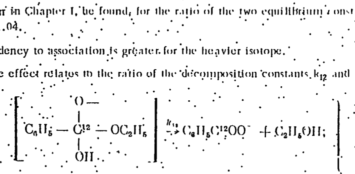


$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + OH^- \rightleftharpoons \left[C_6H_5-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{|}}{C}}-OC_2H_5\right]^- \tag{44}$$

Using the equations given in Chapter I, he found, for the ratio of the two equilibrium constants at the experimental temperature, $K_{12}/K_{14} \approx 1.04$.

As always, the tendency to association is greater for the heavier isotope.

The kinetic isotope effect relates to the ratio of the decomposition constants k_{12} and k_{14} for the enol forms



$$\left.\begin{aligned} &\left[C_6H_5-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O-}{|}}{C^{12}}}-OC_2H_5\right] \xrightarrow{k_{12}} C_6H_5C^{12}OO^- + C_2H_5OH; \\ &\left[C_6H_5-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O-}{|}}{C^{14}}}OC_2H_5\right]^- \xrightarrow{k_{14}} C_6H_5C^{14}OO^- + C_2H_5OH \end{aligned}\right\} \tag{45}$$

In this case $k_{12}/k_{14} > 1$.

Taking as the determining step the rupture of the C – O bond in the enol form, and taking a frequency characteristic for C–O in esters and ethers (ω 1700 cm^{-1}) for this, Bigeleisen found the theoretical value $\alpha_{\text{theor}} = k_{12}/k_{14} = 1.20$. This gives, for the observed values

$$k_{12\text{obs}} : k_{14\text{obs}} = \frac{k_{12\text{theor}}}{K_{12\text{theor}}} : \frac{k_{14\text{theor}}}{K_{14\text{theor}}} = \frac{k_{12\text{theor}}}{k_{12\text{theor}}} \Big/ \frac{K_{12}}{K_{14}} =$$

$$= 1.14 - 1.15, \text{ i.e., } \delta = 0.14 - 0.15.$$

This is almost double the observed value given in recent, more exact determinations [46]

Thus, Bigeleisen did not succeed in obtaining agreement between experimental and calculated values of δ. The reason is probably the incorrect assumption of the intermediate formation of an enol form. As was shown by G.P. Miklukhin [47] the role of tautomeric active forms in chemical reactions and isotopic exchange of hydrogen is smaller than was believed until recently. In particular, the role of enolization of carbonyl compounds was undoubtedly overestimated. Despite this, the above example is instructive with regard to the method of determining the influence of the participation in a reaction of unusual chemical forms, in equilibrium with ordinary molecules, on the magnitude of the isotope effect. In such cases the observed kinetic isotope effect may contain thermodynamic isotopic corrections in concealed form. In cases in which, as in the alkaline hydrolysis of esters, the intermediate equilibrium form is an associated complex, the experimentally observed α

$$\alpha_{\text{kin obs}} = \alpha_{\text{kin theor}} \,/\, \gamma_{\text{thermod}} \tag{46}$$

Conversely, if the active equilibrium form is a dissociation complex,

$$\alpha_{\text{kin obs}} = \alpha_{\text{kin theor}} \ \gamma_{\text{thermod}} \tag{46a}$$

In the kinetics of chemical reactions in solutions many cases are known in which the formation of labile equilibrium forms can be regarded as proved. Thus, in the reactions of acids in aqueous solutions the directly acting agent is the hydroxonium ion H_3^+O, in equilibrium with water and anions

$$HA + H_2O \rightleftarrows H_3^+O + A^- \qquad (47)$$

Acid catalysis, in its turn, commences with the formation of addition complexes with the reacting substances

$$H_3^+O + B \rightleftarrows H_2O + H^+B, \qquad (48)$$

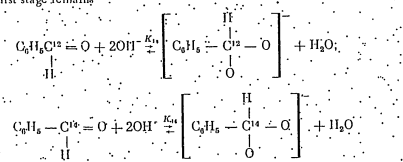
followed by isomerization or decomposition with liberation of H_3^+O

$$\begin{array}{l} H^+B \xrightarrow{H_2O} H_3^+O + B^- \\ \quad \searrow^{H_2O} \\ \qquad H_3^+O + C_1 + C_2 + \ldots \end{array} \qquad (48a)$$

Association complexes are very common; thus, addition complexes are formed with OH^- ions, halide ions, CN^-, etc. In the action of water on mineral oxy-acids and organic carbonyl compounds the formation of ortho-forms is frequently postulated [49, 50]. Finally, there are numerous reactions in which labile forms, in tautomeric equilibrium with more inert forms, react directly. In all such cases thermodynamic isotopic corrections enter into the kinetic isotope effects in hidden form. Their role becomes particularly important when the kinetic constants for the isotopes are equal. Thus, the true kinetic corrections are negligibly small for reactions of C^{12} and C^{14} (or N^{14} and N^{15}) with displacement of hydrogen atoms from some C atoms to others, and for all cases when formation and rupture of similar bonds is the determining step. This probably explains the small value of the isotope effect in the Cannizzaro reaction for benzaldehyde

$$2C_6H_5CHO + H_2O \xrightarrow{OH^-} C_6H_5COOH + C_6H_5CH_2OH \qquad (49)$$

In this case $k_1 = k_2$ (because of the transfer of hydrogen in the determining stage [51]); and only the ratio of the rate constants for the first stage remains



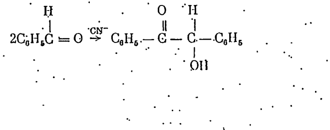
(50)

$$C_6H_5\underset{\displaystyle H}{\underset{|}{C^{12}}} = O + 2OH^- \overset{K_{12}}{\rightleftarrows} \left[C_6H_5 - \overset{\displaystyle H}{\overset{|}{\underset{\displaystyle O}{\underset{|}{C^{12}}}}} - O \right]^- + H_2O;$$

$$C_6H_5 - \underset{\displaystyle H}{\underset{|}{C^{14}}} = O + 2OH^- \overset{K_{14}}{\rightleftarrows} \left[C_6H_5 - \overset{\displaystyle H}{\overset{|}{\underset{\displaystyle O}{\underset{|}{C^{14}}}}} - O \right]^- + H_2O$$

As in the saponification of esters discussed above, the ratio $K_{12}/K_{14} = \gamma$ should be 1.03-1.05.

According to Stevens and Attree [43] and Bigeleisen, the absence of an isotope effect in the benzoin condensation of benzaldehyde in presence of CN^- ions



(51)

$$2C_6H_5\overset{\displaystyle H}{\overset{|}{C}} = O \xrightarrow{CN^-} C_6H_5 - \overset{\displaystyle O}{\overset{\|}{C}} - \overset{\displaystyle H}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}} - C_6H_5$$

is explained by the identical nature of the bonds formed. In this case it is assumed that both in the formation of benzoin with C^{14} in the carbonyl group, and of benzoin with C^{14} in the alcohol group, the determining stage is formation of the $C^{12}-C^{14}$ bond, and therefore $k_{12} = k_{14}$. The thermodynamic isotope effect applies to isotopic isomers, for which it is close to zero; therefore in the reaction product the C^{14} and C^{12} isotopes are uniformly distributed between the ketone and aldehyde carbons.

These examples illustrate the nature of the superposition of thermodynamic and kinetic corrections for reactions in solutions and the existence of a very close relationship between the actual mechanism and the magnitude of these corrections.

§10. Isotope Effects in the Kinetics of Catalytic Reactions

In reaction kinetics it is not easy to determine the boundary between homogeneous catalytic and noncatalytic reactions. No such boundary exists in chain reactions, which form the most extensive type of homogeneous chemical reactions. It is natural that among the reactions discussed in the preceding sections there were many which are overtly or covertly catalytic. Therefore studies of kinetic isotope effects in homogeneous catalysis require, not so much new methods of theoretical analysis or new experimental techniques, as extension of the range of materials studied and greater attention to the catalytic aspects of the problem. The position in heterogeneous catalysis is entirely different. Contact reactions include stages and intermediate forms difficult to characterize quantitatively. For this reason, isotope kinetic effects have been studied little for heterogeneous catalysis and for surface and volume chemical reactions of solids, which are related to it in their mechanisms. An exception is provided by the reactions of heavy hydrogen, which was a favorite object of study in the 1930's. However, at that time the theory of isotope kinetic effects had not been extensively developed, and the level of experimental techniques was considerably lower than it is now. Therefore the fairly extensive experimental data accumulated during the period of general interest in the chemistry of deuterium are generally suitable only for qualitative comparisons and for general orientation. A good review of the data available on the subject in 1943 has been given by Geib [52]. In view of the special features of the experimental material, we shall consider separately the isotopic effects in catalytic reactions of hydrogen and of other elements.

The statistical theory of chemical equilibria and chemical reaction rates is in general applicable to heterogeneous catalysis and to its chemisorption stages. In the simplest cases the factors which determine the occurrence and magnitude of isotope effects in heterogeneous catalysis are the same as in homogeneous reactions. New features are the extensive occurrence of diffusional and mixed diffusional-kinetic regimes; and, in kinetic regimes, the lower certainty concerning the nature of the stages which control the process as a whole and the properties of the breaking or forming surface chemical bonds. This aspect can be regarded as more or less clarified for only a small number of reactions with a few catalysts, but the determinations of isotope kinetic effects in catalysis were usually not made on such systems. Therefore, theoretical interpretation of the results with the aid of statistical methods developed by Bigeleisen, Eyring and others usually lacks sufficient clarity on the nature and properties of the bonds broken or formed at the rate-determining stage. A second difficulty is due to the inhomogeneity of real contact catalysts and absence of direct methods for investigation of vibrational frequencies of adsorption bonds. Their characteristic frequencies ω_0 and ω_0^* are not accurately known for molecules participating in these processes and therefore the values of the zero-point energies $E_0 = \frac{hc\omega_0}{2}$ and $E_0^* = \frac{hc\omega_0^*}{2}$ and of the coefficients u_i and u_i^* in Equations (17), (17a) and (31) cannot be calculated with sufficient accuracy.

In a case in which the determining step is rupture or formation of a definite bond within one of the reacting molecules caused by deformation as the result of interaction with the catalyst, it is not possible to use values of ω_0, ω_0^*, E_0, E_0^*, u_i, u_i^* unconditionally for its characterization. Therefore, until special complex investigations of the simplest model systems have been made, absolute calculations of isotope kinetic effects in heterogeneous catalysis and quantitative verifications of the theoretical relationships are not feasible. However, as will be shown, even qualitative comparisons of the theoretical deductions with experimental data, and rough evaluations of the magnitude of the effects corresponding to different mechanisms, suggest interesting possibilities of utilization of such isotopic corrections in the theory of catalysis.

Dole, Rudd, et al. [53] have recently studied the kinetic isotope effect in the catalytic decomposition of hydrogen peroxide, with manganese dioxide, platinum, colloidal gold, ferric hydroxide, and catalase as catalysts. Winter and Briscoe [54] had already demonstrated the practical absence of oxygen isotope exchange between hydrogen peroxide and water, either on prolonged exposure in solution, or in decomposition in contact with a number of solid catalysts. Dole et al. [53], and also Cahill and Taube [55] confirmed this result and showed that no isotopic exchange takes place between gaseous oxygen and water, or gaseous oxygen and hydrogen peroxide. Since, at low temperatures, the reaction

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (52)$$

is practically irreversible; absence of isotopic exchange between the components should make the isotopic composition of the reaction products (O_2 and H_2O) and of the undecomposed hydrogen peroxide a definite function of the ratio of the decomposition rate constants of $HO^{16}O^{16}H$ and $HO^{16}O^{18}H$ molecules (with a low content of O^{18} the participation of $HO^{18}O^{18}H$ molecules in the decomposition may be neglected*). The content of O^{18} in the O_2 will also depend on the relative probability of the entry of O^{18} into water and into oxygen in the decomposition. Suppose that at a given instant the specific content of O^{18} in the undecomposed part of the H_2O_2, $\rho_{H_2O_2^{18}} = \rho_1$, the specific content of O^{18} in the liberated oxygen $\rho_{O_2^{18}} = \rho_2$, and in the water formed $\rho_{H_2O^{18}} = \rho_3$. The distribution of O^{18} will be determined by two separation factors:

$$\left.\begin{aligned} \alpha_1 &= \rho_2/\rho_1 \\ \alpha_2 &= \rho_2/\rho_3 \end{aligned}\right\} \qquad (53)$$

The first refers to O_2 and H_2O_2, and the second to O_2 and H_2O.

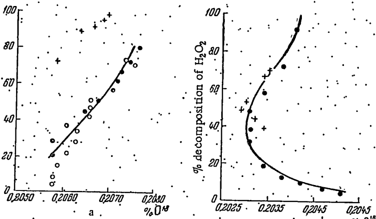


Fig. 59. Integral isotopic composition of oxygen evolved in the catalytic decomposition of hydrogen peroxide at room temperature (22-24°C) [53]: a) MnO_2 catalyst; b) catalase catalyst; ○, ●, + refer to different experiments.

The principal result of a determination of the isotopic composition of the liberated oxygen will be a value of about 1.018 times, or 1.8% higher than the normal value, for the O^{18} content for decomposition in presence of MnO_2, Pt and Au, and 2.3% in presence of $Fe(OH)_3$. In contrast to this, the isotopic composition of oxygen liberated by the action of catalase is similar to the isotopic composition of the oxygen in hydrogen peroxide. A curious fact is that if, instead of ordinary water water enriched with O^{18} is used as the medium, this has no effect at all on the isotopic composition even if the H_2O_2 is almost completely decomposed. This shows that H_2O exchanges not only with the original stable molecules of hydrogen peroxide and the HO_2^- and O_2^{2-} ions in dynamic equilibrium with it, but also with all the intermediate forms such as HO_2, OH, etc., formed in the course of catalytic decomposition. Observations of this kind may be of value for an understanding of the stages in the reaction mechanisms. Fig. 59 shows the variation of the isotopic composition of oxygen with the degree of decomposition in presence of manganese dioxide and of catalase; this shows the high complexity of the latter process.

Values of the individual separation factors may be determined from data of this type. Variations of the isotopic composition of decomposition products with the degree of conversion provide one of the most general methods for calculating isotope effects (see below). In the instance in question, in presence of MnO_2 α_2 is found to be 1.035, and in presence of $Fe(OH)_3$, 1.048. The authors made an interesting attempt to correlate the observed value of the isotope effect with the reaction mechanism. Assuming that heterogeneous decomposition commences with the formation of a hydroxyl radical and ion with the participation of catalyst electrons e_c

$$\left.\begin{aligned} &1)\quad e_c + HO^{16}O^{16}H \xrightarrow{k_1} HO^{16} + O^{16}H^- \\ &2)\quad \phantom{e_c + HO^{16}O^{18}H} \xrightarrow{k_2} HO^{16} + O^{18}H^- \\ &\quad e_c + HO^{16}O^{18}H \\ &3)\quad \phantom{e_c + HO^{16}O^{18}H} \xrightarrow{k_3} HO^{18} + O^{16}H^- \end{aligned}\right\} \qquad (54)$$

Dole et al. postulate the possibility of various consecutive reactions for $O^{16}H$ and $O^{18}H$ radicals:

$$\left.\begin{aligned} &1)\ HO^{16} + HO^{16}O^{16}H \rightarrow H_2O^{16} + O^{16}O^{16}H; \\ &2)\ HO^{18} + HO^{16}O^{16}H \rightarrow H_2O^{18} + O^{16}O^{16}H; \\ &3)\ HO^{16} + HO^{16}O^{18}H \rightarrow H_2O^{16} + O^{16}O^{18}H, \\ &4)\ O^{16}O^{16}H \qquad\quad \rightarrow O^{16}O^{16} + H^+ + e, \\ &5)\ O^{16}O^{18}H \qquad\quad \rightarrow O^{16}O^{18} + H^+ + e; \\ &6)\ H^+ + O^{16}H \qquad \rightarrow H_2O^{16}, \\ &7)\ H^+ + O^{18}H \qquad \rightarrow H_2O^{18} \qquad\qquad \text{etc.} \end{aligned}\right\} \qquad (55)$$

It is further suggested that considerable isotope effects may be observed not only at stages involving rupture of O–O bonds. In the scheme of Dole et al. such a stage is the dissociation of H_2O_2 molecules into HO and OH^- involving a catalyst electron

$$H_2O_2 + e_c \rightarrow HO + OH^-. \qquad (56)$$

On this assumption the magnitude of the isotope effect is determined by the values of the constants k_1, k_2 and k_3 of Equation (54). Starting with the usual simplifications of the Bigeleisen theory and with data on fundamental frequencies of hydrogen peroxide, which have now been thoroughly studied and correlated with a space model, [56-58], Dole et al. calculated the theoretical values of α_1 and α_2 and found 1.078 for the latter. Thus the calculated value of δ was approximately double the experimental value.* There is nothing surprising in this, since neither the sequence of stages chosen by Dole, nor the choice of the determining stage can be regarded as adequately substantiated [59]. Moreover, if rupture and formation of chemisorption bonds with the catalyst is omitted from the determining stage, this inevitably leads to the conclusion that the values of δ are equal (at the same T and with the same solvent and external conditions) for all catalysts which act by the above electron mechanism; however, this is contrary to experience. Nor is it clear why, having assumed the formation of free hydroxyls in the first stage, and of free HO_2 radicals in the second, the authors do not take into account the inevitable occurrence of a volume chain reaction, in accordance with the well established theories of Haber and Willstätter [60], Weiss [61] and others [62].

Thus, the actual numerical result given in this paper is not convincing, but the method of theoretical analysis used is interesting, as are some of the observations. By applying this method of analysis to other actual mechanisms much better agreement between theory and experiment can probably be attained.

We may note that in mechanisms involving formation and rupture of chemisorption surface bonds α and δ will always decrease with increasing atomic weight of the catalyst, and will always be less than in mechanisms involving rupture and formation of ordinary C–C, C–N, and similar bonds. This cannot account for the deviations from the theory in the case of enzyme reactions. The data in the paper in question show a practical absence of an isotope effect in enzymatic decomposition in presence of catalase, and also show the anomalous nature of

---

*For simplicity, the presence of $HO^{17}O^{16}H$ is not considered.

*The latter is 6 times greater than the thermodynamic isotope effects in presence of MnO_2, and 8 times greater in presence of $Fe(OH)_3$.

the variations of the isotopic composition with the degree of decomposition in this reaction. In this connection we must draw attention to the data, cited in §5 of this chapter, obtained by Schmidt, Myerson and Daniels on the enzymatic hydrolysis of urea, for which the values of α and δ were also considerably below the theoretical, while the ratio $\frac{\delta_{C^{12}-C^{14}}}{\delta_{C^{12}-C^{13}}}$ was greatly above the theoretical value of 1.9. The reality of this anomaly is confirmed by the later work of Schmidt and Daniels [63], in which the same reaction

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3 \qquad (57)$$

was studied at a higher temperature and in a weak acid medium (pH 5.0 at 30°C). The ratios of the hydrolysis rate constants, i.e., k_{12}/k_{13} and k_{12}/k_{14} respectively, were calculated from the isotopic composition of carbon in the carbon dioxide for various degrees of conversion of urea, by means of the Downes equation [64]

$$\log\Delta_f = (\alpha - 1)\log(1 - f) + \alpha\log\bar{\Delta} = \delta\log(1 - f) + \alpha\log\bar{\Delta}, \qquad (58)$$

where f is the conversion fraction corresponding to the sample taken for isotopic analysis; $\Delta_f = \frac{[\overset{*}{C}]}{[C^{12}]} \approx \rho(\overset{*}{C})$ in CO_2, i.e., $\Delta_f \approx \rho^*$, the relative content of the tagged isotope in this portion

$$\Delta = \frac{x^*}{x} \qquad (59)$$

In our case this is C^{13}/C^{12} or C^{14}/C^{12} in the CO_2, $\bar{\Delta}$ is the ratio $\frac{x^*}{x}$ in the whole amount of analyzed product, formed when the f-th fraction of the conversion has been reached. The Downes equation is a particular case of more general equations which relate the degree of separation to the degree of conversion and the ratio of the reaction rate constants at different isotopic compositions.*

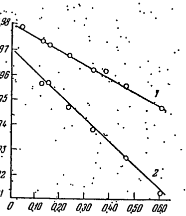


Fig. 60. Separation of carbon isotopes in the course of acid hydrolysis of urea [63]. 1) C^{12}/C^{13}; 2) C^{12}/C^{14}.

Fig. 60 gives the bilogarithmic graph used for calculation of δ and α.

In Table 80, the results for ordinary and enzymatic hydrolysis are compared.

In the theoretical calculation the determining process is taken to be rupture of the C−N bond. For $C^{12}-N^{14}$ the value $\omega = 1008\ cm^{-1}$ is taken, after Kelner [65]. For $C^{13}-N^{14}$ and $C^{14}-N^{14}$ this gives $\omega = 986$ and $\omega = 967\ cm^{-1}$. In calculations by the different approximate formulas of Daniels [66], Eyring and Cagle [35], and others, the agreement between the theoretically calculated results and the experimental data is quite satisfactory for non-enzymatic catalysis, which is a particular case of acid−base catalysis. Data on enzymatic catalysis under the action of urease clearly do not conform to the simplified statistical theory, which is not surprising in view of the great complexity of the kinetics and mechanisms of enzymatic processes. We must emphasize that, for C^{14} at 100°, δ is 3 times as large, and for C^{13} 5.5 times as large without urease, as with urease at 30°C.

On the whole it may be said that the sign and order of magnitude of the kinetic isotope effects for ordinary heterogeneous catalytic reactions and for reactions accelerated by acids and bases are the same as for noncatalytic reactions in solutions. The experimentally determined values of δ on the whole agree with the statistical theory of isotope effects, which serves as additional confirmation of the fundamental principles of the latter. In enzymatic processes, only the sign of the effects is in agreement with the theory. Their magnitude is much less than the theoretical, and other anomalies occur, among them the anomalous ratio of the isotope effects for two carbon isotopes.

---

* Methods for determination of kinetic isotope corrections are described in greater detail in Chapter V.

TABLE 80

Isotope Effects in Urea Hydrolysis, after Schmidt and Daniels

Isotope factor	Enz., 30°C	No enz., 100°C	δ/δ enz.	Theoretical value
αC^{12-14}	1.032	1.101	~3	1.082—1.104
αC^{12-13}	1.010	1.055	~5.5	1.043—1.054
$\delta C^{12-14}/\delta C^{12-13}$	3.2	1.8	0.56	1.9

§11. Kinetic Isotope Effects in Contact Reactions of Hydrogen

Isotope effects in the kinetics of contact gaseous reactions of hydrogen and its compounds have generally been studied without direct reference to the mechanism of the processes. This makes quantitative comparisons with the theory difficult. Moreover, most of the investigations dealing with these systems were published before the statistical theory of isotope effects had been developed fully and before mass spectrometry was extensively used. This is inevitably reflected in the nature of the results.

a) Decomposition of ammonia

Jungers and Taylor [67] obtained a simple and clear picture of the influence of substitution of H by D on the decomposition rate of ammonia. The reaction was studied at 680°C in presence of tungsten wire. In these conditions the decomposition rate of NH_3 is 1.6 times that of ND_3 (Fig. 61). An interesting fact is that the decomposition rate of ammonia containing 48% D lies half way between the decomposition rates of the light and heavy forms. This shows that for the decomposition into nitrogen and hydrogen

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad (60)$$

the rate constants

$$k_{NH_3} > \left.\begin{matrix} k_{ND_2H} \\ k_{NDH_2} \end{matrix}\right\} > k_{ND_3} \qquad (61)$$

From the same data

$$k_{NH_3} = 1.6\ k_{ND_3} \qquad (62)$$

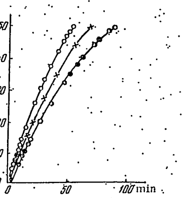


Fig. 61. Decomposition of ammonia in presence of W at 680°C [67]. ○) NH_3; ●) ND_3; x) $N(H,D)_3$−48% D; initial pressure 70 mm Hg.

These data cannot be used to determine the numerical ratios of the rate constants for ammonia molecules with mixed hydrogen isotope compositions to the rate constant for molecules of homogeneous isotopic composition. After the work of Temkin and his school [68-70], the stage mechanism and kinetics of the decomposition of ammonia in presence of metals can be regarded as clarified and generally accepted [71]. The determining step is desorption of activatedly adsorbed nitrogen. The nature of isotopic exchange of nitrogen on metals indicates that undissociated nitrogen molecules are retained in activated adsorption [72, 73]. In this connection the recent work of Taylor and McGeer [74] on the exchange of N and H on rhenium is particularly important, as it explained earlier contradictions. Therefore the determining step may be written as

$$N_{2\,chemis} \rightarrow N_{2\,gas} \qquad (63)$$

The rate constant and activation energy for this process should not change on replacement of protium by deuterium in the ammonia molecule. The most probable explanation of the decrease of the rate by a factor of 1.6, or by nearly 38%, observed by Jungers and Taylor [67] lies in a change of the quasi-equilibrium degree of covering of the tungsten surface by activatedly adsorbed nitrogen, θ_{N_2}. In the modern view, $N_{2\,chemis}$ is in dynamic equilibrium with ammonia and hydrogen [75]

$$N_{2\,ads} + 3H_2 \rightleftharpoons 2NH_3 \tag{64}$$

with an equilibrium constant K, and, because of the energy variations over the surface and changes in the groups of the regions which control the process [76],

$$\vartheta_{N_2} = a\ln\left\{\frac{(NH_3)^2}{K(H_2)^3}\right\} \tag{65}$$

The decomposition rate w, in its turn, is given by the equation

$$w = ke^{+\beta\vartheta_{N_2}} \sim \frac{k}{K^{\beta}}\left[\frac{(NH_3)^2}{(H_2)^3}\right]^{\beta} \tag{66}$$

Equations (65) and (66) contain the equilibrium constant K of Equation (64). This constant differs for different forms of ammonia, and, according to the general rule, it should be higher for deuterated molecules.

$$K_{ND_3} > K_{ND_2H} > K_{NDH_2} > K_{NH_3} \tag{67}$$

The tables in the Appendix can be used to make approximate estimates of the maximum numerical values of the isotope effects for the equilibrium constants. Since, according to Temkin, β is not very far from 0.5, to explain the observed differences it is necessary for the ratio K_{ND_3}/K_{NH_3} to be approximately 2.25. For 680°C, i.e., 953°K, this difference is disproportionately high. The reason for this divergence from the theory is not yet clear.* Some light is thrown on the mechanism of the reaction in question by the work of Singleton, Roberts and Winter, who studied the kinetics of the isotopic exchange of deuterium with ammonia on films of iron, nickel and tungsten, formed by evaporation; and especially by the work of Kemball [78].

b) Oxidation of hydrogen

The kinetics of the catalytic oxidation of H_2 is very peculiar. On active preparations of platinum and palladium at moderate temperatures the rate is directly proportional to the oxygen concentration and inversely proportional to the square root of the hydrogen concentration [79, 80]

$$w = k\frac{[O_2]}{\sqrt{[H_2]}} \tag{68}$$

At very low temperatures (−76°C) and above 300°C the kinetic relationships are different [80].

Catalyst activity is very sensitive to the content of oxygen in the metal, and may be increased by heating in gaseous oxygen and decreased by heating in hydrogen [81]. The catalytic reaction is itself capable of activating catalysts which had previously not been activated by oxygen to the maximum value [79-81]. Because of these peculiarities, it is not easy to obtain strictly reproducible and readily comparable results. It is not surprising that there is no complete agreement between the data of different authors on the magnitude of the isotope kinetic effects. According to Melville [82], in the temperature range from 160 to 250°C and under pressures from 1 to 760 mm Hg, $\alpha \doteq 2$. An interesting fact is that exactly the same value for $\alpha = k_1 : k_2$ under similar conditions was also obtained by the same author for the oxidation of hydrogen by nitrous oxide in presence of nickel [83]

$$\left.\begin{aligned} N_2O + H_2 &\xrightarrow{k_1} N_2 + H_2O \\ N_2O + D_2 &\xrightarrow{k_2} N_2 + D_2O \end{aligned}\right\} \tag{69}$$

In the more detailed investigation performed by Tucholsky [84] with the use of palladium, large values of α (1.85!) were observed only at 20°C. At 200°C, α fell to 1.1, and finally, with palladium previously brought into contact

---

* The calculated value of δ would agree with the experimental value if the determining step included rupture or formation of N−H bonds, but this would require revision of the scheme as a whole. If the NH_3 decomposition rate is highly sensitive to impurities, the discrepancy between δ_{exp} and δ_{theor} can also be attributed to differences in the purity of the gas.

with O_2 at 200-380°C, α = 1, that is, there was no isotope effect. For the reaction carried out under the same conditions, but with preliminary admission of hydrogen, α = 1.1.

According to our data, heating of Pd to 200-380°C in oxygen activates while heating in hydrogen deactivates it. There are also serious grounds for considering chemisorption of oxygen to be the determining step [85]. With such a mechanism α should be 1. Small deviations of α from 1 after hydrogen treatment might be attributed to differences in the rates of removal of deuterium and ordinary hydrogen, which inhibit the reaction, from the metal. It might be possible to explain similarly the results obtained by Tucholski for palladium when the prepared mixture was admitted into the reaction vessel in the temperature range 20-200°C. It is not clear whether Melville's results could be explained in this way, as the determining step on nickel is not necessarily the same as on palladium. Since Melville's experiments were performed at higher pressures, there may have been diffusional hindrances, which by themselves could give $\alpha = \sqrt{D_2} : \sqrt{H_2}$, i.e., 1.4; finally, the experimental technique of kinetic investigations was often not at a high level in the 1934-1936 researches. Because of all this a repetition of the work on isotope effects in the catalytic oxidation of H_2 is desirable, with modern requirements and the peculiarities of the reaction mechanism taken into account.

c) Other gaseous catalytic reactions

Many investigations have dealt with comparisons of the rates of catalytic hydrogenation by light and heavy hydrogen. Most of them involved the hydrogenation of ethylene. A serious complicating factor in this case is isotopic exchange between the unsaturated compound and hydrogen. This was not taken into account in the earliest studies. The same complication remains in the hydrogenation of acetylene, higher unbranched olefins, and most aromatic compounds.

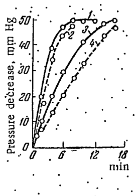


Fig. 62a. Reaction rates of ethylene at 40°C in presence of Cu [86] (50 mm C_2H_4; 50 mm H_2): 1) $C_2D_4 + H_2$; 2) $C_2H_4 + H_2$; 3) $C_2D_4 + D_2$; 4) $C_2H_4 + D_2$.

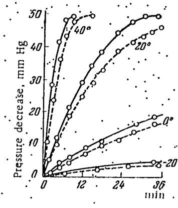


Fig. 62b. Effect of temperature on reaction rates: ---- $H_2 + C_2H_4$, —— $H_2 + C_2D_4$.

According to Joris, Jungers and Taylor [86], in hydrogenation by heavy hydrogen over copper, two opposing factors must be taken into account: replacement of H by D in the olefin molecule, which accelerates addition both of light and heavy hydrogen, and transition from H_2 to D_2 which retards the process. It is evident that the existence of isotopic exchange unrelated to the hydrogenation can lead to confusion. Fig. 62 gives kinetic curves for hydrogenation (deuteration) of ethylene molecules of different isotopic composition. Later investigations showed that absolutely pure copper at low temperatures has practically no catalytic effect on the hydrogenation, and the power of copper of ordinary purity to act as a hydrogenation catalyst is due to the presence of small amounts of nickel [87]. It is therefore probable that the active agent in the catalyst used by Joris, Taylor and Jungers, which consisted of copper on magnesium oxide, was nickel. Unfortunately, a direct comparison of the hydrogenation of C_2H_4 and C_2D_4 over metallic nickel was not made.

Tucholski and Rideal [88] compared the hydrogenation of ordinary ethylene by light and heavy hydrogen over nickel. At temperatures of 0-40°C, α was found to be 1.6. At 140°C, α was 1.1, and at 180°, unexpectedly,

TABLE 81

Kinetic Isotope Effects for Heterogeneous Hydrogen Reactions (after Geib [52])

Reactions of light hydrogen	Corresponding reactions of deuterium	Catalyst	T, °C	Pressure, (mm Hg)	Ratio of rate constants $k_1 : k_2$
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Cu	0	760	2
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Cu (+ MgO)	20	100	2
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Cu (+ MgO)	40	100	2.5
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Fe	30—50	~1	1.9—2.4
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Fe	50—80	~1	2.4—1.5
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Ni	0 (—40)	10	1.6
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Ni	140	10	1.4
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Ni	180	10	1
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Cu (+MgO) old cat.	−20, +20, +40	100	0.75
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Cu (+MgO) fresh cat.	—30, +20, +40	100	1
$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_2H_4 + D_2 \rightarrow C_2H_4D_2$	Pt	26	50	1.5
$C_2H_2 + H_2 \rightarrow C_2H_4$	$C_2H_2 + D_2 \rightarrow C_2H_2D_2$	Pt	0	—	1
$CH_3COCH_3 + H_2 \rightarrow (CH_3)_2CHOH$	$CH_3COCH_3 + D_2 \rightarrow (CH_3)_2CDOD$	Pd	20—200	8	1.85—1.1
$O_2 + 2H_2 \rightarrow 2H_2O$	$O_2 + 2D_2 \rightarrow 2D_2O$	Pd, H (D)	200—380	8	1.10
$O_2 + 2H_2 \rightarrow 2H_2O$	$O_2 + 2D_2 \rightarrow 2D_2O$	Pd, O	200—380	8	1.00
$O_2 + 2H_2 \rightarrow 2H_2O$	$O_2 + 2D_2 \rightarrow 2D_2O$	Ni	160—250	7 — 760	2
$O_2 + 2H_2 \rightarrow 2H_2O$	$O_2 + 2D_2 \rightarrow 2D_2O$	Ni	160—250	1 — 760	2
$N_2O + H_2 \rightarrow H_2O + N_2$	$N_2O + D_2 \rightarrow D_2O + N_2$	W	~680	35—150	1.6
$2NH_3 \rightarrow N_2 + 3H_2$	$2ND_3 \rightarrow N_2 + 3D_2$	—	20	—	1
$CuO + H \rightarrow Cu$	$CuO + D \rightarrow Cu$	—	156—269	—	1.26—1.1
$CuO + H_2 \rightarrow Cu + H_2O$	$CuO + HD \rightarrow Cu + HDO$	—	370—440	—	>1
$2AgCl + H_2 \rightarrow 2Ag + 2HCl$	$2AgCl + D_2 \rightarrow 2Ag + 2DCl$	Pt (sol)	—	—	>1
$H_2O_2 \rightarrow \frac{1}{2}O_2 + H_2O$	$D_2O_2 \rightarrow \frac{1}{2}O_2 + D_2O$				

α 1. The hydrogenation was carried out at 10 mm Hg *

The isotope effect in presence of metallic iron was studied by Klar [89], who observed, at p   1 mm Hg, in the temperature range 30 to 80°C, a very peculiar variation of α with a maximum of the order of 2.5 at about 50°C (Fig. 63). It is very difficult to explain this maximum on the basis of the statistical theory. Geib [52] suggested that this is a false maximum of α, caused by superposition of isotopic exchange for C_2H_4 and D_2. Geib's review gives no direct proof in favor of this explanation.

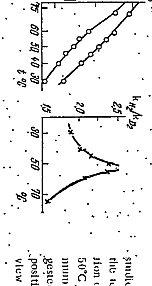


Fig. 63. Effects of temperature on the rate constant and on the ratio of the rate constants for the hydrogenation of ethylene by light and heavy hydrogen over iron powder [89].

In summarizing the results of this far-from-complete review of isotope effects in the catalysis of reactions of hydrogen and its compounds, we may note that although these effects are large, generally in the range 1.5-2, they are nevertheless smaller than for homogeneous reactions of hydrogen, and generally do not exceed the magnitude of the thermodynamic isotopic corrections. It is therefore legitimate to regard as causes of the differences, in addition to kinetic effects in the true sense, the isotopic corrections for hidden adsorptional and chemical equilibria. In this connection we refer again to the theoretical discussion in Chapter I, and to the data obtained by Melkonian and Reps [90], who found a separation factor of 3 for H_2/D_2 mixtures on desorption from silica gel at the temperature of liquid air. It is not clear whether serious importance should be attached to the frequently observed sharp sensitivity of α to the experimental conditions, or to the nature and purity of the catalyst. This question seems worthy of a more detailed investigation, as it may prove that it conceals new potentialities for the investigation of catalysts and catalytic processes. Finally, we may note that even under pure diffusion conditions the rates of the reactions of H, D and T should be in the ratio 1 : 0.704 : 0.58, or $k_H : k_D \approx 1.42$ and $k_H : k_T \approx 1.73$.

Table 81 contains a summary of data (after Geib [52]) on kinetic isotope effects of heterogeneous hydrogen reactions.

§ 12. Kinetic Isotope Effects of Processes Related to Heterogeneous Catalysis

a) Adsorption

Fairly considerable kinetic isotope effects have often been observed in activated adsorption. As an example, we may cite the kinetic graph from the paper by Beebe et al. [91] (Fig. 64): Fig. 64 gives isotherms for the adsorption of H_2 and D_2 on metallic copper obtained by reduction of copper oxide in a current of hydrogen at 120-170°C. The hydrogen was admitted by portions every 30 minutes. Curves 1 and 2 were obtained with 16-minute intervals before the admission of each new portion, and Curve 3, with 12 hours.

The natural interpretation of the graph is as follows. In 12 hours there is time for true adsorption equilibrium to be established, which is practically the same for deuterium and ordinary hydrogen. In 16 minutes there is not enough time for equilibrium to be established, and therefore Curves 1 and 2 are pseudoisotherms, which show differences in the adsorption rates for D_2 and H_2. By varying the holding time and the experimental temperature, it is possible both to intensify and to diminish the differences between the two isotopic forms of hydrogen. In the experimental conditions represented by Fig. 64, H_2 was adsorbed more rapidly than D_2.

As is known, several forms of hydrogen sorption are known – molecular or van der Waals adsorption, chemisorption, and occlusion. Hydrogen may undergo chemisorption in different ways on the same surface. In addition,

---

*This jump in the value of α was possibly caused by a 20° difference in the positions of the rate optima in hydrogenation with D_2 and H_2. Since above 140° the rate of H_2 addition decreases, while the rate of D_2 addition continues to increase approximately to 160°C, α should fall sharply between 140 and 160°C. However, the origin of the optimum hydrogenation temperature is itself not completely clear, and therefore a rational explanation of the shift in the optimum cannot be given. Thus, this observation establishes a connection between two obscure phenomena, but does not explain either of them.

TABLE 82

Comparison of the Adsorption Rates of H_2 and D_2

Adsorbent	T, °C	Pressure, mm. Hg	Ratio of rate constants $\alpha = k_{H_2}:k_{D_2}$	Literature
Pt	−80—+50	760	1.4 1.5	[92]
Cu	0	2.63	5.5	[91]
	125	2.63	1	
	71—153 −171	5	1.00 −1.32—1.25	[93]
Ni	−112—−45	1.55	1.4—1.17	[94]
	9 25	0.2 1.2	1.36 1.15	[95]
	0—30	~1	>1	[95]
	30—100	~1	>1—1	
Ni on SiO_2	101—184	760	1	[96]
Cr_2O_3 and $Cr_2O_3 \cdot ZnO$	101—184	760	1	
Cr_2O_3	150—210	760	1	[97]
Fe	80—120	~1	≥1	[95]

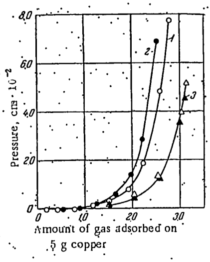


Fig. 64. Isotherms for adsorption of hydrogen and deuterium on copper at −78°C [91].

○ H_2 } Held 16 minutes before admis-
● D_2 } sion of a portion of gas

△ H_2 } Held 12 hours
▲ D_2 }

there are several forms of occlusion: formation of true solid solutions adsorption on internal intercrystallite boundaries, and solution in the surface layer. The variety of forms, in conjunction with the possibility of different hydromechanical and thermal conditions, may lead to sharp differences in the values of α found in the same investigation under different conditions. A further source of differences in comparisons of the results of different investigations is unequal chemical purity and structure of the adsorbents. Therefore, good reproducibility cannot be expected. The table above, taken from Geib's review with some simplifications, shows kinetic isotope effects in hydrogen adsorption.

Table 82 gives data on the adsorption rates of H_2 and D_2 on a number of typical catalysts for reactions of the oxidation—reduction type: platinum, copper, ordinary and deposited nickel, iron, chromium oxide, and chromium oxide with zinc oxide. In one instance only (Cu at 0°C) does α appreciably exceed the ratio $(m_H/m_D)^{-1/2}$, and therefore some of the data might be explained by differences of the coefficients of diffusion (volume or surface) caused by differences of mass. Arguments against this interpretation are the sharp and sometimes very peculiar dependence of α on temperature (for example, for Cu), and the fact that α is unity for several systems. For a clear understanding of these phenomena, more detailed and more differentiated determinations are needed, which take into full account the greatly increased information on the kinetics and mechanism of hydrogen adsorption.

b) Desorption

Isotope effects are more pronounced in desorption than in adsorption. The primary reason for this is the existence of an activation energy in molecular, nonspecific adsorption, which coincides with the heat of adsorption, so that the determinations can be made at extremely low temperatures. However, at low temperatures thermodynamic isotopic corrections increase also, and it is not easy to distinguish between true kinetic and hidden thermodynamic corrections.

Isolated and qualitative observations on the partial separation of different isotopic forms of hydrogen during desorption are contained in numerous publications of the 1930's [98, 99]. Among the publications of this period, special mention should be made of the work of Peters and Lomas [100]. Table 83 gives typical results of one of their experiments, in which active carbon was used.

TABLE 83

Separation of Isotopic Hydrogen Molecules in Desorption [100]

Initial equilibrium concentrations at 25°C	H_2	HD	D_2
	81.5	17.0	1.5
Fraction 1	100.0	0.0	0.0
2	100.0	0.0	0.0
3	65.3	36.5	0.0
4	0.0	93.5	6.5

In the experimental conditions, the observed separation could have been caused either directly by differences in the desorption rates, or by differences in the plane diffusion rate from the pores to the outer surfaces of the adsorbent particles.

A more thorough study of this effect was made by Harteck and his associates [101, 102] who showed that the separation coefficients are higher on silica gel than on active carbon, and that these coefficients increase rapidly with decreased surface cover and temperature. This was shown particularly clearly by Harteck and Melkonian [103]. At the temperature of liquid hydrogen (−253°C) and high degrees of surface covering the separation coefficient is 20. When the adsorption is decreased to 37.8 cc/g, the value increases suddenly to 100. Such values of α exceed the thermodynamic coefficients calculated from zero-point energies and heats of adsorption. In the careful investigation of Melkonian and Reps [90], a comparison with the adsorption isotherms for ordinary hydrogen gave the value ΔQ_{ads} 500—600 cal/mole for the difference of the heats of adsorption. The determinations were performed at −195 and −183°C with adsorptions of the order of 0.01 cc/g. The values of the equilibrium constants for the isotopic exchange of D_2 and H_2 between the adsorbate and the gas, determined at different temperatures, satisfy the equation

$$K = 0.21 \cdot e^{480/RT} \tag{70}$$

The authors identify this difference (480 cal/mole) with the difference of the zero-point energies in the adsorbed state, $\Delta Q = \Delta E_0$. At moderate and high degrees of adsorption ΔE_0 is considerably lower. According to Formula (70) and experimental data for −195°C K = 4.5, and for −183°C K = 3.0. Much higher separation coefficients are obtained in rapid desorption; these cannot be explained even by introduction of the additional factor $\sqrt{2}$, to allow for the difference of diffusion rates. The authors therefore postulate an appreciable kinetic factor in the true sense of the word, equal to about 1.2. The kinetic factor in its usual meaning also includes the diffusion factor, i.e., $\alpha_{kin} = 1.7$. Previous energy "smoothing" of the surface by adsorption of CO_2 decreases the value of the thermodynamic isotopic coefficient, somewhat increasing the kinetic. With such high separation coefficients for molecular hydrogen and deuterium it would be natural to expect appreciable effects also for molecules not differing so sharply in mass. However, attempts to detect kinetic desorption effects for isotopic HCl molecules and for mixtures of light and heavy methane have so far been without result, probably because of unsuitably chosen experimental conditions. The possibility of appreciable isotope effects in the desorption of hydrogen has not been sufficiently taken into account in numerous studies of the o → p conversion and isotopic exchange of hydrogen at the temperature of liquid air and at even lower temperatures.

c) Diffusion of hydrogen through metals

It is often difficult to draw a boundary between adsorption and volume solution of gases in solids. The kinetics of these processes, usually controlled by diffusion in the crystal lattice, is well understood. As in adsorption, it is necessary here to distinguish between nonspecific occlusion, such as the sorption of inert gases and hydrocarbons by zeolites, and chemical solution. For a dissolved gas the mobility is characterized by the diffusion coefficient. Isotope effects in this process have been repeatedly studied for various metals, and the differences have been found to be relatively small. As an example, we will quote the results of a recent very thorough study of the diffusion of deuterium and hydrogen in pure metallic zirconium [104]. The diffusion is of an activated nature, the activation energy being the same for light and heavy hydrogen. The ratio of the diffusion coefficients is

$$\frac{D_{H_2} = 1.09\cdot 10^{-3}\cdot e^{-11\,400/RT}}{D_{D_2} = 0.73\cdot 10^{-3}\cdot e^{-11\,400/RT}} = 1.5$$

This is near to $\sqrt{2}$ 1.414. It seems that 11400 cal/mole is expended in creating gaps in the lattice through which the diffusion occurs, the dissolved hydrogen is completely dissociated into atoms, and the zero-point energy of its bonds does not affect the rate either directly or indirectly. On these assumptions the difference in the diffusion rates of the isotopes should be completely determined by the difference of their masses, and the ratio of the diffusion coefficients should be the same as in free diffusion of H and D atoms in a gas.

Similar observations are also available for other metals; for example, in the old paper by Jost and Widman this value for Pd is 1.35 [105]; and for Pt 1.33 [105a]; for tritium the retardation of diffusion is still greater with increase of the ratio $\sqrt{T} : \sqrt{H}$.

d) Topochemical reactions

If gases or liquid solutions are involved in addition to solids in topochemical reactions, differences in the reaction rates of the isotopes appear in the same way as in homogeneous or heterogeneous catalytic reactions, by changes in the isotope ratios in the phases of variable composition. In reactions which occur with solids only, isotope effects may appear as deviations from equipartition of the isotopes between phases. Isotope effects in such reactions have been studied little; and it is difficult to draw a boundary between thermodynamic and kinetic effects. We shall therefore consider reactions of the first type only.

The simplest, but relatively rare, type of topochemical process, used for the production of active solids, is a chemical reaction of a gas or vapor which proceeds with formation of a solid phase. For example, in some studies of catalyst structure zinc oxide and magnesium oxide were prepared by combustion of zinc and magnesium vapors. Catalysts may be prepared by decomposition and oxidation of organometallic compounds [106].

Metallic nickel made by decomposition of nickel carbonyl has interesting catalytic properties. The formation and decomposition of dicobalt octacarbonyl, $Co_2(CO)_8$, have recently become of great importance in connection with various reactions of organic molecules with mixtures of CO and H_2 [107].

Kinetic isotope effects in reactions of this type have been studied in detail by Bernstein [108] for the decomposition of nickel tetracarbonyl tagged with C^{14}. The kinetics of this reaction is fairly well understood [109, 111]. The decomposition rate is given by the equation

$$-\frac{d\,[Ni(CO)_4]}{dt} = \frac{k_1\,[Ni\,(CO)_4]}{1 + k_2\,[CO]}, \qquad (71)$$

which at low carbon monoxide concentrations, when $k_2\,[CO] \ll 1$, becomes a first order equation

$$-\frac{d\,[Ni\,(CO)_4]}{dt} = k_1\,[Ni\,(CO)_4], \qquad (72)$$

and at high concentrations, when $k_2\,[CO] \gg 1$, it passes into Equation (73).

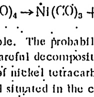
$$-\frac{d\,[Ni\,(CO)_4]}{dt} = \frac{k_1}{k_2}\,\frac{[Ni\,(CO)_4]}{[CO]}. \qquad (73)$$

The observed activation energy of the process decreases in the transition from (72) to (73). The materials used in the investigation contained a natural admixture of heavy carbon, i.e., about 1.1% C^{13} of the total carbon content. With such a low content of the tagged isotope, it is sufficient in considering the isotope effects to take into account only the decomposition of nickel carbonyl molecules not containing C^{13} and of molecules containing one C^{13} atom each, i.e., $Ni(C^{12}O)_4$ and $Ni(C^{12}O)_3\cdot(C^{13}O)$. Molecules tagged with two or more C^{13} atoms each are too rare.

The final decomposition products are metallic nickel and carbon monoxide. It was long ago found from kinetic data [109, 110] that the rate of the first decomposition step is determined by the removal of one (the first) molecule of carbon monoxide from nickel carbonyl according to the equation

$$Ni(CO)_4 \rightarrow Ni\,(CO)_3 + CO \qquad (74)$$

with an activation energy of about 11000 cal/mole. The probability of this mechanism is confirmed by data on the decomposition kinetics of cobalt carbonyl, careful decomposition of which [107] yields the tricarbonyl in the form of the tetramer $[Co(CO)_3]_4$. The structure of nickel tetracarbonyl is completely symmetrical, and the carbon monoxide molecules are joined to the nickel situated in the center of the molecule. The type of bonds is not quite clear, but in any event the monoxide molecules are linked to the nickel through carbon. By the ordinary octet scheme, the presence of four electron pair bonds $OC : \overset{CO}{\underset{CO}{\ddot{\underset{\cdot\cdot}{Ni}}}} : CO$ should be expected, which, in the classical theory of valence is equivalent to



$$\begin{array}{c} CO \\ | \\ OC{-}Ni{-}CO \\ | \\ CO \end{array}$$

Sometimes double bonds are postulated both between nickel and carbon, and between carbon and oxygen $O = C = \overset{C\,=\,O}{\underset{C\,=\,O}{\overset{\|}{\underset{\|}{Ni}}}} = C = O$, but such schemes do not satisfactorily convey the characteristics of the electronic structure of the transitional metal carbonyls, in the formation of which d-electrons play an important part. Four Ni−C bonds are directed to the corners of the tetrahedron containing the nickel atom at its center. The strict tetrahedral structure is practically undisturbed if one, two, or more molecules of $C^{12}O$ in the carbonyl are replaced by $C^{13}O$ or $C^{14}O$, but the symmetry numbers change sharply.

On the assumption that the removal of one molecule of carbon monoxide is the determining step, it is natural to base the calculations of isotope effects on the rupture of one nickel−carbon bond. Because of the unstable nature of $Ni(CO)_3$ it has not yet proved possible to isolate this intermediate product and determine its carbon isotope composition; and therefore control of the isotope separation has to be restricted to studies of the isotope composition of the carbon monoxide and the remaining undecomposed nickel tetracarbonyl. It is therefore not possible to separate directly the intramolecular isotope effect, which is equal to

$$\alpha_{intramol} = \frac{k_3}{3k_2}, \qquad (75)$$

from the intermolecular isotope effect

$$\alpha_{intermol} = \frac{k_1}{4k_2}. \qquad (75a)$$

The meaning of the rate constants k_1, k_2 and k_3 in Equations (71 - 73) and (75) is clear from the scheme for the primary decomposition reactions.

$$Ni(CO)_4 \xrightarrow{k_1} Ni(CO)_3 + CO$$

$$Ni(CO)_3\dot{C}O \rightarrow \begin{cases} \xrightarrow{k_2} Ni(CO)_3 + \dot{C}O \\ \xrightarrow{k_3} Ni(CO)_2(\dot{C}O) + CO \end{cases} \tag{74a}$$

By this scheme

$$\frac{d}{dt}[CO] = 4k_1[Ni(CO_4)] + 3(k_2 + k_3)[Ni(CO)_3(\dot{C}O)];$$

$$\frac{d}{dt}[\dot{C}O] = (k_2 + k_3)[Ni(CO)_3(\dot{C}O)],$$

and hence

$$\frac{[CO]}{[\dot{C}O]} = 3 + 4\left(\frac{k_1}{k_2 + k_3}\right)\frac{[Ni(CO)_4]}{[Ni(CO)_3(\dot{C}O)]} \tag{76}$$

With a normal content of C^{13} in the original carbonyl ($\gamma = 0.011$)

$$\alpha = 1 + \delta = \frac{[CO]}{[\dot{C}O]} \Big/ \frac{1-\gamma}{\gamma}, \tag{76a}$$

where $\frac{[CO]}{[\dot{C}O]}$ is the ratio $\frac{C^{12}}{C^{13}}$ in the carbon monoxide liberated in the reaction. This expression, since γ is small, can to a good degree of approximation be replaced by

$$\alpha = k_1/(k_2 + k_3) \tag{76b}$$

The magnitude of the intramolecular effect does not depend on the temperature, and is given by the expression

$$\alpha_{intramol} = \frac{k_3}{3k_2} = \left(\frac{m^*}{m}\right)^{1/2} \tag{77}$$

Substitution of the numerical values of m and m* for $Ni-C^{12}$ and $Ni-C^{13}$ gives the calculated value for $\alpha_{intramol} = 1.0345$. For the intermolecular effect.

$$\alpha_{intermol} = \frac{k_1}{4k_2} = \left(\frac{m^*}{m}\right)^{1/2}[1 + \Sigma G(u_i)\Delta u_i - \Sigma G(u_i^*)\Delta u_i^*] = \left(\frac{m^*}{m}\right)^{1/2}[1 + \psi] \doteq \alpha_{intramol}[1 + \psi(T)] \tag{77a*}$$

Having assumed the relationship between u_i and the fundamental frequencies of the Ni−C bond, and using the notation of Crawford and Cross [112], the author finds the values given in Table 84 for the two stretching frequencies of the $Ni-C^{12}$ and $Ni-C^{13}$ bonds, their differences $\Delta\omega$, and the corresponding values for C−O bonds.

The values of ψ_1 given in Table 85 are obtained for the part of the isotope effect ψ which depends on the temperature, with only the terms relating to the original molecules taken into account; the details of this calculation, which involves the decrease of symmetry in the transition from $Ni(CO)_4$ to $Ni(CO)_3(\dot{C}O)$, will not be discussed here.

The same table gives the experimental values ψ_{expt}, found from the dependence of the experimental values of $\alpha = \frac{k_1}{k_2 + k_3}$ on the temperature. The table contains smoothed values, corresponding to points on a straight line obtained by the method of least squares, and not the results of individual determinations, the reproducibility of which is not high.

---

*It follows from the equation $\alpha = 1 + \delta$ that $\psi \doteq \frac{\alpha - \nabla}{\nabla} \doteq \nabla^{-1}(1 + \delta) - 1$ or $\delta = \nabla \times (1 + \psi) - 1$, where ∇ is the fraction $(m^*/m)^{1/2}$.

TABLE 84

Characteristic Frequencies of $Ni(CO)_4$ Molecules

Designation*	$Ni-C_{str}$		$C-O_{str}$		Note
	$\omega_1(a_1)$	$\omega_2(f_2)$	$\omega_1(a_1)$	$\omega_2(f_2)$	
Found [112]	380	300	2040	2050	Bernstein's calculation [108] includes the correction of a small error in the previous publication [112].
Calculated for $Ni(C^{12}O)_4$	382.1	339.5	2043.6	2044.0	
Calculated for $Ni(C^{13}O)_4$	376.0	331.7	1994.6	1998.7	
$\Delta\omega_{calc}$	6.1	7.8	49.0	46.2	

TABLE 85

Comparison of Experimental and Theoretical Values of ψ for the Decomposition of $Ni(CO)_4$; ψ_1 Calculated for Constant ω_{CO}; ψ_2 Calculated on the Assumption of a 5% Decrease of ω_{CO} in the Intermediate Complex

T, °C	ψ_1	ψ_{expt}	ψ_2
25	0.0044	0.0119	0.0101
50	0.0037	0.0103	0.0088
75	0.0032	0.0086	0.0079
100	0.0028	0.0069	0.0072
125	0.0025	0.0052	0.0066

The straight line $\alpha = \alpha(T)$ can be represented by the equation

$$\alpha = \frac{k_1}{k_2 + k_3} = 1.0222 - 6.7 \times 10^{-5}T(°C) \tag{78}$$

It is easily seen that the corrections to ψ_1 calculated from the frequencies of the Ni−C bonds are 2–3 times smaller than the experimental values. Allowance for u_i^* and Δu_i^* would only increase the discrepancy between the theoretical and experimental values. A totally different result is obtained if it is assumed that, in addition to rupture of Ni−C bonds, some weakening of carbon−oxygen bonds occurs during the determining step. This correction to Slater's model of the rupture of isolated independent bonds, because of the high value of the isotope effect for the C−O bond, on the assumption of a 5% change in ω_{CO} in the intermediate complex (with corresponding corrections introduced into ψ), results in almost complete agreement between the calculated values (see the ψ_2 column in Table 85) and the theoretical data. This is a very instructive result, but it has been achieved by the introduction of a correction of arbitrary magnitude. If ω_{CO} was changed even by 8% instead of 5%, ψ_2 would be appreciably larger than ψ_{expt}. It is possible that the true cause of the deviation is that the topochemical nature of the process was not taken into account. We also give an empirical expression for the intermolecular effect

$$\alpha_{intermol} = \frac{k_1}{4k_2} = 1.0481 - 6.7 \cdot 10^{-5}T\ (°C)$$

This expression is obtained from Equation (78) after elimination of $\alpha_{intramol}$. Bernstein's work shows that the

---

* No caption appears in the original – Translator.

decomposition of $Ni(CO)_4$ is in general agreement with the theory, but calculations based on the simplest version of the theory do not yield the experimental numerical values. For a correct interpretation of the results it would be interesting to carry out parallel determinations of the isotopic composition of nickel tricarbonyl in the course of the reaction, and also to repeat the work with $Ni(CO)_4$ tagged with C^{14} so that $\alpha_{C^{13}}$ and $\alpha_{C^{14}}$ could be compared.

Topochemical reactions of solids involving gases, of the following type, are very common

$$\left.\begin{array}{l} A_s + gas_1 \rightarrow B_s + gas_2; \\ A_s \rightarrow B_s + gas. \end{array}\right\} \qquad (79)$$

Isotope effects for reactions of this type have been studied, for the reduction of copper oxide to metallic copper by ordinary hydrogen and deuterium [93].

$$\left.\begin{array}{l} CuO + H_2 \rightarrow Cu + H_2O; \\ CuO + HD \rightarrow Cu + DHO \end{array}\right\} \qquad (80)$$

As the temperature increased from 156 to 269°C $k_H : k_D$ fell from 1.26 to 1.11. According to the results of the same researches, the rate constants for the reduction of copper oxide by atomic hydrogen and atomic deuterium at room temperature are practically the same. Even a simple difference in the number of collisions should give a 1.4-fold difference. It is possible that the equal values of the rates indicate that in this case the determining step is some step which occurs without direct participation of hydrogen.

§ 13. Comparative Action of Hydrogen Isotopes in Acid–Base Catalysis

In many of the reactions in solution, discussed in §4 and 5 of this chapter, hydronium or hydroxyl ions participate in overt or covert form. As was shown, variations of the carbon and nitrogen isotope composition influence the rates of these reactions in accordance with the statistical theory of kinetic isotope effects. The magnitude of these effects is not great, in no instance exceeding 20%. They are primarily interesting in that they reflect the mechanisms of the determining steps of the processes. Differences in the rates of acid–base catalysis caused by substitution of heavy hydrogen for light are usually greater than this. The effects caused by replacement of protium by tritium are even greater. Such effects cannot be ignored even in rough exploratory studies. They introduce appreciable corrections into the kinetic isotope exchange equation and result in appreciable isotope separation.

A distinction is made between acid–base catalysis in the true classical sense of the term, in which transfer of a hydrogen ion* (H^+ or D^+ or T^+) is an obligatory step, and acid–base catalysis in the broader electronic sense [113] which may involve substances which do not contain hydrogen, acting as acids. For considering the effects of hydrogen isotopes it is natural to use the concepts of acids and bases introduced by Bronsted and Lowry, and the protolytic steps introduced by them [113]. According to Bronsted and Lowry, an acid is any form capable of donating a hydrogen ion, and a base is any form capable of accepting a hydrogen ion. Many authors have discussed the mechanism of acid–base catalysis on the basis of these concepts, and very many investigations in the 1930's and 1940's were devoted to experimental studies of the mechanism and kinetics of acid–base catalysis in water and other solvents. Since a presentation of the theory of acid–base catalysis is outside the scope of the present book, we shall confine ourselves by a reference to the extensive reviews made at various times on this subject [113–117]. It should be noted, however, that the modern views on the inner mechanism of protolysis differ appreciably from those of Bronsted. For example, a much smaller role is ascribed to reversible dissociation. Acidic and basic properties are directly related to the electronic structure of the corresponding substances. An important role in the transfer of protons from acids to bases is attributed to intermediate formation of hydrogen bonds, which join the reacting molecules into unstable association complexes, within which hydrogen transfer occurs. In order to avoid the difficulties which are involved in the use of modernized protolytic schemes, we shall use the Bronsted theory in its classical form.

---

*It is usual to refer to proton transfer, protolytic reactions, etc.; in the present instance this terminology is inconvenient for comparing the action of H with D and T, and it is avoided as far as possible.

In this theory a distinction is made between general catalysis by acids and bases, in which all the molecular species present in a solution, with acidic and basic properties in the Bronsted sense, appreciably accelerate a particular process, and specific acid or specific base catalysis, in which only hydroxonium or only hydroxyl ions, respectively, accelerate the process. General acid–base catalysis is more common than special acid or base catalysis, which may be regarded as the limiting case with very great predominance of one of the two forms. Since the catalysts are unchanged in such reactions, it follows that any sequence of steps should be in the nature of a closed cycle with respect to the catalyst, and therefore in cases in which catalysis commences with the loss of a hydrogen ion by the catalyst, it must terminate with the addition of a new hydrogen ion to the residue, or vice versa.

In acid–base catalysis it is necessary to distinguish between processes in the analysis of the rates of which it is sufficient to take into account one transfer of a hydrogen ion between the catalyst and the catalyzed substance, and processes in which two hydrogen ion transfers must be taken into account.* We shall denote the catalyzed substance (substrate) by S, the acid catalyst by A, and the base formed when A loses one hydrogen ion by B. Then the following expressions are valid for protium, deuterium, and tritium acids

$$\left.\begin{array}{l} a)\ A = B + H^+; \\ b)\ A = B + D^+; \\ c)\ A = B + T^+ \end{array}\right\} \qquad (81)$$

A, B and S may be neutral or positively or negatively charged, but the charge of B is always one positive unit less than the charge of A

Acid catalysis with one proton transfer may be represented as follows:

$$\left.\begin{array}{ll} a,\ b) & S + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SH^{\oplus} + B \\ c) & SH^{\oplus} \xrightarrow[k_2]{} X. \end{array}\right\} \qquad (82)$$

Completely analogous expressions may be written for deuterium and tritium, containing, instead of $SH^{\oplus}$, $SD^{\oplus}$ and $ST^{\oplus}$ respectively. In this expression X is the final product of the catalytic conversion, and the transition from $SH^{\oplus}$ to X is assumed to be irreversible. This representation does not exclude the participation of other molecules of S, or of other molecules S_1 and S_2, in the conversion.

Let us define the nature of $SH^{\oplus}$ rather more closely. It is the addition product of a proton and a substrate molecule. Hydrogen ions can be added to many substances because of their small size and the consequent anomalously large value of electrostatic potential

$$V = \frac{e}{r}. \qquad (83)$$

The addition occurs particularly easily with atoms of molecules containing unshared pairs in the electron shells, such as with oxygen in inorganic and organic compounds, trivalent nitrogen, sulfide sulfur, and halogens. Thus, water yields hydronium ions $H_3O^{\oplus}$, ammonia and amines give ammonium ions $NH_4^{\oplus}$, $RNH_3^{\oplus}$, ethyl alcohol gives $C_2H_5OH_2^{\oplus}$ etc. The presence of double bonds between C atoms or between C and N facilitates the addition. As was shown in Chapter III, fully saturated and aromatic hydrocarbons give highly unstable compounds of the carbonium type: $CH_3^{\oplus}$; $C_3H_7^{\oplus}$; $C_6H_7^{\oplus}$, etc.

Equation (82) is highly schematic, as it does not take into account the solvating action of the solvent and the presence, in most cases, not only of the specially added acid A and the corresponding base B, but also of solvent molecules with acidic and basic properties, and the reaction products of A and B with the solvent, which can act as additional acids and bases. The situation is somewhat simplified in reactions in solvents with very low dielectric constants, such as hydrocarbons.

---

*In a complete scheme of stages there are always at least two hydrogen ion transfers, but with a monohydrogen mechanism, the second transfer, which restores the catalyst to its original state, occurs rapidly as a side reaction which does not affect the rate or kinetics. Processes with three or more proton transfers are also possible.

Generally speaking, in catalysis the concentrations of A and B should not change, and therefore, if we neglect the slight effect of changes in the medium caused by the reaction on the rate constants, the relationship between the three rate constants: k_1', k_{-1}' and k_2, which are directly related to k_1 and k_{-1} (see below) must be regarded as determining the kinetics. It can be shown that in general acid–base catalysis, involving one hydrogen ion transfer from A to S, this transfer determines the rate of the whole process. We shall demonstrate this for a particular combination of rate constants. Let

$$k_1 \ll k_{-1}, \tag{84}$$

so that S is a much weaker base than B. Because of the inequality (84), the concentration $[SH^{\oplus}]$ is small in comparison with the concentrations [S] and [A]. It is therefore legitimate, using Bodenstein's method of quasistationary concentrations, to assume that the rates of formation and consumption of $SH^{\oplus}$ are equal

$$w_{\text{form}} = k_1 [S] [A] = w_{\text{cons}} = k_{-1} [SH^{\oplus}] [B] + k_2 [SH^{\oplus}] \tag{85}$$
$$k_1' [S] = k'_{-1} [SH^{\oplus}] + k_2 [SH^{\oplus}].$$

In passing to Equation (85) we introduced, instead of k_1 and k_{-1}, new rate constants for the forward and reverse processes, k_1' $k_1[A]$ and k'_{-1} $k'_{-1}[B]$. From Equation (85)

$$[SH^{+}] = \frac{k_1' [S]}{k'_{-1} + k_2}, \tag{86}$$

and the rate of formation of the reaction product X is

$$\frac{d[X]}{dt} = k_2 [SH^{+}] = \frac{k_2 k_1'}{k'_{-1} + k_2} [S] \tag{87}$$

It follows that the reaction should be of the first order with respect to the substrate with the rate constant

$$k_{\text{acid}} = k = \frac{k_2 k_1'}{k'_{-1} + k_2} \tag{88}$$

Suppose further that $k_2 \gg k'_{-1}$; then in the equation for <u>k</u> we can reject k'_{-1} in the denominator and cancel k_2 in the numerator and denominator. As a result

$$k = k_1' \tag{89}$$

and

$$\frac{d[X]}{dt} = k_1^1 [S] = k_1 [S] [A]. \tag{90}$$

The rate of reaction catalyzed by the acid A coincides with the rate of hydrogen ion transfer from A to S.

A similar analysis may be applied to catalysis by a base. In this case we shall indicate the corresponding kinetic constants by the sign °.

$$\left.\begin{array}{c} S + B' \underset{°k_{-1}}{\overset{°k_1}{\rightleftarrows}} R^{\ominus} + A; \\ R^{\ominus} \xrightarrow{°k_2} X, \end{array}\right\} \tag{91}$$

where $R^{\ominus}$ is a molecule of S which has lost one proton. With neutral S, $R^{\ominus}$ is a univalent anion, if S has one positive charge $R^{\ominus}$ is neutral, etc. It is evident that when $°k_1 \ll °k_{-1}$, i.e., when $R^{\ominus}$ is a much weaker base than B,

$$[R^{\ominus}] = \frac{°k_1' [S]}{°k_{-1} + °k_2}; \tag{92}$$

$$k_{\text{base}} = k = \frac{°k_2 \cdot °k_1'}{°k'_{-1} + °k_2} \tag{93}$$

and when $°k_2 \gg °k'_{-1}$.

$$\frac{d[X]}{dt} = °k_1' [S] = °k_1 [S] [B] \tag{94}$$

Thus, in this case the rate of the whole process of base catalysis is also determined by the rate of proton transfer, but in this instance from S to B, and not from A to S as in acid catalysis.

According to the Bigeleisen–Slater theory of kinetic isotope effects, the rate-determining step is the rupture of the bond attached to the isotope in the original molecule or in the molecule of the equilibrium intermediate substance. In the present instance, for acid catalysis it is natural to consider the rupture of a $B-H^{+}$ bond in a molecule of A, and in base catalysis, the rupture of an $R^{-}-H^{+}$ bond in a molecule of S. As was pointed out in Chapter I, the force constants for bonds differing only in isotopic composition are practically equal, but the reduced masses μ are greater for bonds containing the heavier isotope, and therefore

$$\mu_{L-T} > \mu_{L-D} > \mu_{L-H} \tag{95}$$

where L is the atom directly linked to the transferred hydrogen ion in the catalyzing acid or in the substrate, therefore the frequencies

$$\omega_i = \frac{1}{2\pi c} \sqrt{\frac{P_i}{\mu_i}}$$

(see Equation (56) in Chapter I) and the corresponding zero-point energies E_{0i} $\frac{hc\omega_i}{2}$ will be in the sequence

$$E_{0L-H} > E_{0L-D} > E_{0L-T} \tag{96}$$

Inequality (96) leads to two other inequalities; for the bond dissociation energy D, and for the energy E of the formation of the intermediate activation complex

$$D_{L-H} < D_{L-D} < D_{L-T}; \tag{97}$$
$$E_{L-H} < E_{L-D} < E_{L-T} \tag{98}$$

Both the frequencies of adiabatic transfer, and the probability of tunnel leakage through the barrier, should increase with decreasing isotope mass, and therefore we can say in general that for the two types of processes in question it is always true that

$$k_H^{\text{obs}} > k_D^{\text{obs}} > k_T^{\text{obs}} \tag{99}$$

The situation is quite different with a relatively slow conversion of the intermediate active form $SH^{\oplus}$ (in acid catalysis) or $R^{\ominus}$ (in base catalysis). Let us consider the limiting case

$$k_2 \ll k_{-1}, \tag{100}$$

or, correspondingly,

$$^{\circ}k_2 \ll {}^{\circ}k_{-1} \qquad (100a)$$

With this relationship between k_2 and k_{-1} the intermediate form is in equilibrium with the substrate and the catalyst

$$\left.\begin{array}{l} a)\ S + A \rightleftarrows SH^{\oplus} + B \text{ with } K_{\text{acid}} = \dfrac{[SH^{\oplus}][B]}{[S][A]}; \\ b)\ S^{\ominus} + B \rightleftarrows R^{\ominus} + A \text{ with } K_{\text{base}} = \dfrac{[R^{\ominus}][A]}{[S^{\ominus}][B]} \end{array}\right\} \qquad (101)$$

Evidently,

$$[SH^{\oplus}] = K_{\text{acid}} \frac{[S][A]}{[B]} \qquad (102)$$

and

$$[R^{\oplus}] = K_{\text{base}} \frac{[S^{\oplus}][B]}{[A]} \qquad (102a)$$

Hence

$$\omega_{\text{acid cat}} = k_2[SH^{\oplus}] = k_2 K'_{\text{acid}}[S]; \qquad (103)$$

$$w_{\text{base cat}} = {}^{\circ}k_2[R^{\ominus}] = {}^{\circ}k_2 K'_{\text{acid}}[S^{\ominus}] \qquad (103a)$$

In both cases under consideration the reaction is of the first order

$$w = k[S], \qquad (104)$$

But the constant k contains the product of two constants sensitive to the isotopic composition: the kinetic constant k_2 and the equilibrium constant K. The first of these decreases on substitution of protium by deuterium and of deuterium by tritium. It is natural to expect that, depending on the structure of the molecules involved in the equilibrium and on the ratio of the fundamental frequencies of the bonds linking the hydrogen atoms in A_H and $SH^{\oplus}$ or A_D and $SD^{\oplus}$ respectively, the equilibrium constant K may, in some reactions, increase with transition to a heavier hydrogen isotope, and in other reactions decrease in such a transition. When

$$K_H > K_D > K_T, \qquad (105)$$

the experimentally observed rate constant

$$k_H^{obs} = k_{2H} K_H. \qquad (106)$$

should always be greater than

$$k_D^{obs} = k_{2D} K_D; \qquad (106a)$$

and, correspondingly, k_D^{obs} should be greater than

$$k_T^{obs} = k_{2T} K_T. \qquad (106b)$$

In this instance the condition (99) is satisfied, and reactions determined by hydrogen ion transfer can be distinguished from reactions determined by decomposition of the intermediate equilibrium form only by the magnitude of the isotope effect. It is probable that in aqueous solutions it is always true that $K_D > K_H$ and $K_T > K_D$, and therefore the case just considered is of no interest for these. When

$$K_T > K_D > K_H \qquad (105a)$$

the thermodynamic and kinetic isotope effects are of opposite sign.

If, at the same time, the absolute magnitude of the thermodynamic isotope effect is greater than the absolute value of the kinetic isotope effect, then the relationship between the observed rate constants for analogous reactions with different isotopes will be unusual

$$k_T^{obs} > k_D^{obs} > k_H^{obs} \qquad (105b)$$

This is the predominant situation in acid catalysis in aqueous solutions.

An increase of the rate of acid–base catalysis on replacement of light by heavy hydrogen isotopes is impossible for reactions determined by hydrogen ion transfer, and (105b) conclusively shows that the determining step is decomposition of the intermediate complex $SH^{\oplus}$ or $R^{\ominus}$ respectively. If the absolute magnitude of the thermodynamic isotope effect is less than that of the kinetic isotope effect, and of opposite sign, we have the already familiar situation

$$k_H^{obs} > k_D^{obs} > k_T^{obs}, \qquad (99)$$

but with smaller differences between the observed rate constants. Inequality (99) is typical for base catalysis.

To sum up, we may conclude that replacement of light by heavy hydrogen in acid–base catalysis may result both in acceleration and in retardation. The first provides a definite indication of the nature of the determining step, but the second may occur with different types of determining steps. When $k_H > k_D > k_T$, it may be possible to determine the stages more precisely from the numerical values of the isotope effects. However, this only gives reliable information with considerable differences between the kinetic isotope effects calculated from the Bigeleisen–Slater theory and the experimentally observed values. Finally, it should be noted that since an anomalous course of k is always the result of subtraction of two effects, while a normal course may be obtained without subtraction and even by addition of the kinetic and the thermodynamic effects, in general the differences between the rates should be greater with a normal course than with an anamalous course of the constants.

Acid–base catalysis contains numerous examples or processes with two hydrogen ion transfers, which, for protons, may be schematically represented as follows:

$$\text{Acid catalysis} \qquad HR \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (HRH)^{\oplus} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} RH. \qquad (107)$$

$$\text{Base catalysis} \qquad HR \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R^{\ominus} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} RH. \qquad (107a)$$

Since in Equations (107), (107a) it is important to show the position of hydrogen, instead of S and S' we write HR and RH. In the mechanism with two hydrogen ion transfers, isomerization with displacement of double bonds and hydrogen, or isomerization with ring opening or closing, often occurs. It is probable that in such reactions the transfers of two hydrogen ions occur consecutively as distinct steps; however, some authors support the possibility of simultaneous coordinated removal of one hydrogen ion in one part of the molecule with addition of another hydrogen ion in another part of the molecule. This triple mechanism has been postulated by Lowry [118], Ingold [119], and Swain [120].

For reactions with two hydrogen transfers, the analysis of isotope effects is still more complicated, and comparisons with the theory are impossible without detailed kinetic data. In our literature, isotope effects in acid–base catalysis have been discussed by G.P. Miklukhin [121] and A.I. Brodsky [49]. Detailed theoretical analyses of the problem have been made by Schwarzenbach [122] and by Reitz [123].

Table 86 gives the ratios of the observed rate constants for acid catalysis, and Table 87 the ratios for base catalysis, in heavy and light water, taken mainly from the excellent if somewhat out of date review by Reitz [124]. For numerical data, reference should be made to these tables; we shall now consider some individual examples which illustrate the general relationships.

TABLE 86

Acid Catalysis in Heavy Water

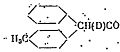
Reaction	T, °C	Catalyst	k_D/k_H	Literature
Inversion of cane sugar	25	H_3O^+, D_3O^+	2.0_5	[125, 126]
Mutarotation of d-glucose	25	H_3O^+, D_3O^+	0.7_3	[127, 128]
		Acetic acid	0.4	[128]
Hydrolysis of acetal	18	H_3O^+, D_3O^+	2.6_4	[129]
Hydrolysis of ethyl orthoformate	18	H_3O^+, D_3O^+	2.0_5	[130, 131]
Hydrolysis of methyl acetate	15	H_3O^+, D_3O^+	1.6	[132]
Hydrolysis of ethyl acetate	15	H_3O^+, D_3O^+	1.5	[133]
Hydrolysis of ethyl formate	15	H_3O^+, D_3O^+	1.4	[132]
Hydrolysis of acetamide	25	H_3O^+, D_3O^+ 0.1-4.0 n.	1.5-0.8_5	[134]
Hydrolysis of acetonitrile	105	H_3O^+, D_3O^+	1.36	[134]
Bromination of acetone:				
CH_3COCH_3 CD_3COCD_3	25	H_3O^+, D_3O^+	2.1	[135, 132]
CH_3COCH_3	25	Monochloroacetic acid	0.8	[136]
CH_3COCH_3	25	Acetic and other acids	0.7	
Decomposition of diazoacetic ester	0	H_3O^+, D_3O^+	3.4	[137]
	15		3.1_5	
	25-35		2.9	
Isomerization of acinitroethane	5	H_3O^+, D_3O^+	1.0	[138]
Depolymerization of dihydroxyacetone	0	H_3O^+, D_3O^+	1.1	[139]
Decomposition of dithionic acid	40-100	H_3O^+, D_3O^+	2.5-2.2	[140]
Oxidation of bromide by bromate		H_3O^+, D_3O^+	2.5	[143, 144]
Oxidation of chloride by bromate		H_3O^+, D_3O^+	3.5	
Oxidation of iodide by bromate		H_3O^+, D_3O^+	2.4	
Oxidation of bromide by iodate		H_3O^+, D_3O^+	4.0-7.0	
Oxidation of iodide by iodate		H_3O^+, D_3O^+	~10	
Decarbonization of mesityl aldehyde		H_2SO_4 100%	0.41	[140]
		60%	1.8	
Decomposition of 1-benzoyl-2-cyano-1,2-dihydroquinoline to benzaldehyde	80	H_2SO_4-t	0.19	[140]

a) Halogenation of ketones

This reaction type, which is of practical importance, has been studied in detail by numerous workers, mainly for the bromination and iodination of acetone. Quantitative data are available for the halogenation of ordinary acetone CH_3COCH_3, and completely deuterated heavy acetone CD_3COCD_3. Under the same external conditions at room temperature both light and heavy acetone are brominated 2.1 times as rapidly in presence of D_3O^+ as in presence of H_3O^+. The reaction is accelerated not only by hydronium ions, but by other acids (see Table 86), the numerical value of the isotope effect varying with the catalyst. Halogenation is also greatly accelerated by bases. In such cases as Table 87 shows, $k_D : k_H > 1$. As long ago as 1904 Lapworth discovered, for the halogenation of

TABLE 87

Base Catalysis in Heavy Water

Reaction	T, °C	Catalyst	k_D/k_H	Literature
		Hydrolysis in heavy water		
Saponification of ethyl acetate	15	(OH^-, OD^-)	1.33	[141]
Hydrolysis of monochloroacetate	45	(OH^-, OD^-)	1.2	[142]
Hydrolysis of acetamide	25	(OH^-, OD^-)	0.9_0	[134]
Hydrolysis of acetonitrile	35	(OH^-, OD^-)	1.2_0	[134]
Hydrolysis of diacetone alcohol	15	(OH^-, OD^-)	1.45	[129, 132]
True base catalysis: comparison of rates in H_2O and in D_2O				
Mutarotation of d-glucose	25	H_2O, D_2O	0.26	[127-145]
	25	CH_3COO^-	0.42	
Decomposition of nitramide NH_2NO_2/ND_2NO_2	25	H_2O, D_2O	0.19	[128, 146, 147]
	15	H_2O, D_2O	0.26	[148]
In solution:				
(91.5% D_2O)	15	CH_3COO^-	0.42	[140]
(91.5% D_2O)	15	$C_6H_5COO^-$	0.45	
(91.5% D_2O)	15	Salicylate	0.16	
Neutralization of nitroethane in H_2O: $C_2H_5NO_2$; in D_2O: $CH_3CH_2NO_2$ (1st stage)	5	OH^-, OD^-	1.40	[150]
$C_2H_5NO_2$, CH_3CHDNO_2 (2nd stage)	5		0.5	[149]
$C_2H_5NO_2$, CH_3CDNO_2 (3rd stage	0		0.15-0.4	
Neutralization of nitroisopropane $C_3H_7NO_2$ in H_2O and in D_2O (1st stage)	5	OH^-, OD^-	1.36	[150]
Bromination of nitromethane	25	CH_3COO^-	0.8_5-0.9	[151]
	25	CH_2ClCOO^-	0.7-0.8_5	
	70	H_2O, D_2O	~0.5	
Bromination of acetone	25	CH_3COO^-	0.9	[136]
Comparison of rates for ordinary and deuterated compounds in the same solvents				
Enolization of 2-o-carboxybenzylindane-2-one	24-25	CH_3COO^-	0.2_3-0.3_3	[152]
Neutralization of nitroethane $CH_3CH_2NO_2$ and CH_3CHDNO_2 in D_2O	0	OD^-	0.3_7	[150]
$CH_3CH_2NO_2$ and $CH_3CD_2NO_2$ in D_2O	0	OD^-	0.1-0.2_5	[146]
Bromination of nitroethane CH_3NO_2 and CD_3NO_2 in H_2O	25	CH_3COO^-	0.14-0.16	[151]
	25	CH_2ClCOO^-	0.19-0.23	
	70	H_2O	0.20-0.26	
Bromination of acetone CH_3COCH_3 and CD_3COCD_3	25	CH_3COO^-	0.1_5	[136]
Racemization of 	100	OH^-	0.22	[153]

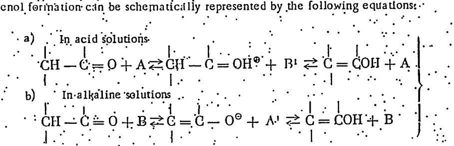
acetone, two remarkable characteristics of such reactions: 1) the reaction rates of bromination and iodination, under the same conditions, are equal; 2) the rate does not depend on the free halogen concentration [154]. To explain these and some other peculiarities of the process, Lapworth postulated that not the ordinary keto form is brominated, but its enol isomer, formed reversibly according to the equation

$$CH_3-CO-CH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_2=COHCH_3, \tag{108}$$

or, for heavy acetone

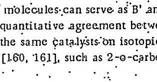
$$CD_3-CO-CD_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CD_2=CODCD_3. \tag{108a}$$

This viewpoint was developed by Dawson [155] and others, who showed that it is applicable to the halogenation of other carbonyl compounds [156, 157], and also to the halogenation of acetone by N-halogen compounds in hydrocarbon solutions [158], when the stage mechanism is simplified because of the absence of acidic or basic properties in the solvent molecules. In simple ketones the equilibrium concentration of the enol form is very low; being only about 10^{-4} % [159]. The reaction falls into the class of general acid–base catalysis. More detailed investigations showed that, in reactions in alkaline solutions, the intermediate form is not the enol but the enolate ion, and the process of enol formation can be schematically represented by the following equations:

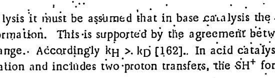


$$\left.\begin{array}{l}\text{a) In acid solutions}\\ -\overset{|}{\underset{|}{C}}H-\overset{|}{C}=O+A\rightleftarrows-\overset{|}{\underset{|}{C}}H-\overset{|}{C}=OH^{\oplus}+B'\rightleftarrows\overset{|}{\underset{|}{C}}=\overset{|}{C}OH+A\\ \text{b) In alkaline solutions}\\ -\overset{|}{\underset{|}{C}}H-\overset{|}{C}=O+B\rightleftarrows\overset{|}{\underset{|}{C}}=\overset{|}{C}-O^{\ominus}+A'\rightleftarrows\overset{|}{\underset{|}{C}}=\overset{|}{C}OH+B\end{array}\right\} \tag{109}$$

The first represents the process in presence of an acid (A), and the second, in presence of a base (B). In both cases the oxygen obtains the hydrogen of the enolate hydroxyl not by direct transfer from an adjacent carbon atom, but from the acid A, shown as such in Equation (109a) and as (A') in Equation (109b). In acid catalysis, the base B takes hydrogen from C–H. Water molecules can serve as B' and A'. The correctness of the enol (enolate) bromination scheme is confirmed by the quantitative agreement between the accelerating action of acids and bases on halogenation, and the action of the same catalysts on isotopic exchange with deuterium in water, and on racemization of optically active ketones [160, 161], such as 2-o-carboxybenzylindane-1-one



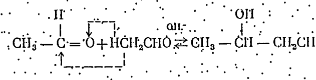
On the basis of kinetic analysis it must be assumed that in base catalysis the determining step in halogenation is proton transfer in anion formation. This is supported by the agreement between the rates of halogenation, racemization, and isotopic exchange. Accordingly $k_H > k_D$ [162]. In acid catalysis of the same reaction, the process passes through enol formation and includes two proton transfers, the SH^+ formed at the first stage



$$\gt CH-\overset{|}{C}=O+A\rightleftarrows \gt CH-\overset{|}{C}=OH^{+}+B \tag{110}$$

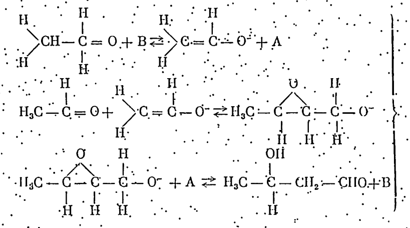
being in equilibrium with the ketone and the acid, and the observed rate is determined by the rate of the subsequent more difficult process of hydrogen ion removal from the $\gt CH-\overset{|}{C}=OH^+$ group. Therefore the isotope effect is determined by the ratio of the products $k_D\cdot K_D$ and $k_H\cdot K_H$ [163]. The observed rate constants are smaller in light than in heavy water, $k_D^{obs} > k_H^{obs}$.

Enols and enolate ions also constitute the intermediate active forms in other reactions of ketones, including aldol condensation



$$CH_3-\overset{H}{\overset{|}{C}}=O+HCH_2CHO\overset{OH^-}{\rightleftarrows}CH_3-\overset{OH}{\overset{|}{C}H}-CH_2CHO,$$

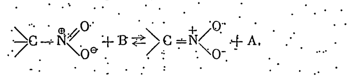
for which the following stages have been postulated [134]:



$$\left.\begin{array}{l}{H\atop H}\!\!\gt CH-\overset{H}{\underset{H}{C}}=O+B\rightleftarrows{H\atop H}\!\!\gt C=\overset{H}{C}-O^-+A\\ H_3C-\overset{H}{C}=O+{H\atop H}\!\!\gt C=\overset{H}{C}-O^-\rightleftarrows H_3C-\overset{O}{\overbrace{\underset{H}{C}-\underset{H}{C}}}-\overset{H}{\underset{H}{C}}-O^-\\ H_3C-\overset{O}{\overbrace{\underset{H}{C}-\underset{H}{C}}}-\overset{H}{\underset{H}{C}}-O^-+A\rightleftarrows H_3C-\overset{OH}{\underset{H}{C}}-CH_2-CHO+B\end{array}\right\} \tag{111}$$

Naturally, this reaction also resembles halogenation in its isotope effects in acid and basic media [134].

In halogenation kinetics and isotope effects, halogenation of nitroparaffins in many respects resembles halogenation of ketones. A characteristic distinction of the former is that they are not susceptible to the catalytic action of acids in aqueous solutions. This is to be expected, since the nitro group is more acidic than the carbonyl group and has no tendency to add on hydrogen ions. Originally, the active intermediate form was considered to be the aci-nitro form $\gt C=\overset{\oplus}{N}\left\langle{OH \atop O^{\ominus}}\right.$, present in tautomeric equilibrium in very low concentrations [164]. However, it is more likely to be the ion $\gt C=\overset{+}{N}\left\langle{O^- \atop O^-}\right.$, formed according to the equation



$$\gt C-\overset{\oplus}{N}\left\langle{=O \atop O^{\ominus}}\right.+B\rightleftarrows\gt C=\overset{+}{N}\left\langle{O^- \atop O^-}\right.+A. \tag{112}$$

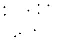
The bromination of nitromethane has been studied in greater detail than other similar reactions. When catalyzed by acetate ions, the rates of isotopic exchange and bromination are equal [161]. A similar agreement was also found between the bromination and racemization rates of optically active nitro compounds [165]. In accordance with the theory, the bromination rate of nitromethane, catalyzed by bases, is lower in heavy than in light water (see Table 87), and the ratio k_D/k_H is from 0.5 to 0.9 in different cases. We may note that this table does not contain corrections for differences between H_2O and D_2O in acidic and basic properties, and therefore it shows not the true k_D/k_H ratios, but the ratio of the directly observed constants k_D/k_H.

b) Nitration of aromatic compounds

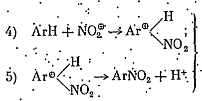
As a second example of homogeneous reactions of the acid–base type, the mechanism of which was determined by measurement of the isotope effect for hydrogen, we shall now consider the nitration of aromatic hydrocarbons. Such reactions are generally carried out with the aid of a nitration mixture consisting of nitric and sulfuric acids, and more rarely with nitric acid alone, or with nitrogen oxides [166]. Depending on the composition of the nitration agent, temperature, and other conditions, different numbers of nitro groups (NO_2) can be introduced into the benzene ring. A study of the kinetics of the reaction of toluene nitration, in conjunction with earlier data [167, 168], led Ingold and his associates to postulate the intermediate formation of the nitronium ion NO_2^+, which is the direct nitrating agent. The process may be represented by the following stages.

A. Formation of a nitronium ion from two HNO_3 molecules or from one molecule of HNO_3 and one molecule of H_2SO_4:

$$\left.\begin{array}{ll} 1) & 2HNO_3 \rightarrow H_2NO_3^{\oplus} + NO_3^{\ominus}; \\ 1a) & HNO_3 + H_2SO_4 \rightarrow H_2NO_3^{\oplus} + HSO_4^{\ominus}; \\ 2) & H_2NO_3^{\oplus} + NO_3^{\ominus} \rightarrow 2HNO_3; \\ 2a) & H_2NO_3^{\oplus} + HSO_4^{\ominus} \rightarrow HNO_3 + H_2SO_4; \\ 3) & O_2\overset{\oplus}{N}OH_2 \rightarrow O_2N^{\oplus} + H_2O, \end{array}\right\} \qquad (113)$$

i.e., first a hydrogen ion is added to give the aci nitro form with the structure  $O_2N-O\overset{+H}{-}H$, and the latter then decomposes to give a nitronium ion NO_2^+ and water. It is assumed that the first process is reversible, while the second may occur practically irreversibly.

B. Nitration of the aromatic compound ArH, represented as two bimolecular steps:



$$\left.\begin{array}{ll} 4) & ArH + NO_2^{\oplus} \rightarrow Ar^{\oplus}\begin{matrix} H \\ NO_2 \end{matrix}; \\ 5) & Ar^{\oplus}\begin{matrix} H \\ NO_2 \end{matrix} \rightarrow ArNO_2 + H^+ \end{array}\right\} \qquad (113a)$$

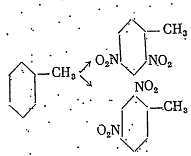
or a single-step trimolecular process:

$$\left.\begin{array}{ll} 6) & NO_2^{\oplus} + ArH + NO_3^{\ominus} \rightarrow ArNO_2 + HNO_3; \\ 6a) & NO_2^{\oplus} + ArH + HSO_4^{\ominus} \rightarrow ArNO_2 + H_2SO_4. \end{array}\right\} \qquad (113b)$$

The first half of Scheme (A) is confirmed by the retardation of the nitration rate by NO_3^- ions according to a hyperbolic law

$$w \approx [NO_3^-]^{-1} \qquad (114)$$

without a change in the reaction order. Confirmation of this scheme with a more precise determination of the rate-determining step was provided by Melander's experiments with tagged tritium [169]. These experiments were performed with toluene in conditions in which, practically, only 2,4-dinitrotoluene is formed; i.e., the substitution



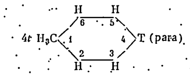
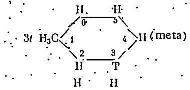
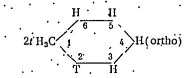
(115)

occurs in the ortho- and para-positions. In some of the experiments tritium was added to the nitration mixture, consisting of 1 volume of concentrated nitric acid and 2 volumes of concentrated sulfuric acid. Radiometric determinations showed that in these experiments the nitration product, after removal of solvent, contained no tritium. Consequently, in these concentrated solutions neither the hydrogen of the phenyl group, nor the hydrogen of the methyl group, exchange with hydrogen of the solvent. The second series of experiments was performed with toluene containing tritium in different positions in the aromatic nucleus [170].

Data for 4t- and 3t-toluene (Table 88) show an absence of intramolecular isotopic exchange during nitration, either in the phenyl group or between C_6H_5 and CH_3. The fact that 50% of the tritium was retained after nitration of the 2t-form in which, because of the low tritium content, only molecules with one tritium atom in position 2 are present (the second position 2 is always occupied by H), indicates a practical absence of an isotope effect despite the enormous difference between the masses of tritium and hydrogen. It follows from this that Reactions 1), 1a), 5) and 6), in which bonds with hydrogen are broken or hydrogen is transferred, cannot be rate-determining. The remaining stages are 3) and 4), a common feature of which is absence of changes of the total charge of the system. The validity of this view is confirmed by the results of Ingold and his school on the weak influence of a change of solvents even when there are large differences between their dielectric constants. The absence of isotopic exchange between hydrogen and toluene in acid solutions makes impossible any additional quasi-equilibrium involving H in the nitration process. Since the rates of substitution of protium and tritium in the nucleus are equal, Reaction 5) must be rejected, and this leads to the conclusion that Reaction 4) is the determining step. Here Reaction 3) in its turn can influence the rate of $O_2N^{\oplus}$ formation (or its equilibrium concentration), but in Melander's experiments reactions generating $NO_2^{\oplus}$ could not have had an influence. Additional information on the mechanism of nitration is contained in the paper by Bennet et al. [171] and in Ingold's monograph [172]. By skillful use of isotope effects and isotopic exchange it has proved possible to clarify the mechanism of this practically very important group of reactions.

TABLE 88

Percentage of the Original Tritium Retained in 2,4-Dinitrotoluene After Nitration of Monotritiated Toluene [170]

Position of tritium in the nitrated compound	Theoretical, %	Experimental %	Notes
	0	2.2	Due to other nitration products present as impurities
	100	99 0	
	50*	51 9; 49.7 (two experiments)	On the assumption that the nitration rates of C-T and C-H are equal

A considerable number of investigations have dealt with the effect of the deuterium content of water on isotope effects in acid and base catalysis. A rare example of a linear relationship between the rate constant and the D_2O content is provided by the mutarotation of glucose. This, together with the anomalous ratio of the rate constants for acid catalysis in heavy and light water, $k_D/k_H < 1$, indicates simple proton transfer.

Nonlinear curves are typical for acid catalysis; an example is provided by the relationship for k_n/k_h in the inversion of cane sugar (Fig. 65), where k_n is the rate constant for a mole fraction of D_2O - n, and k_h is the rate constant in ordinary water. The same relationship has been studied in differential form for the bromination of acetone, catalyzed by hydrogen ions. In this case it proved possible to determine the individual variations of k_H and k_D with the percentage composition of D_2O. Curves for the bromination of light (Curve I) and heavy (Curve II)

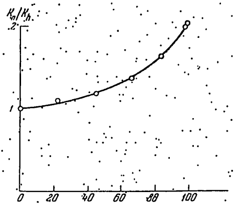


Fig. 65. Variation of the rate constant for the inversion of cane sugar in aqueous solution with the D_2O content.

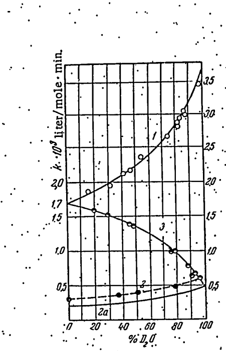


Fig. 66. Variation of the rate constant of acetone bromination, catalyzed by hydrogen ions, with the D_2O content in the water. 1) Light acetone CH_3COCH_3; 2) heavy acetone CD_3COCD_3; 3) "equilibrium" H−D acetone.

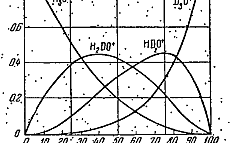


Fig. 67. Variation of the concentrations of various oxonium ions with the D_2O content in a solution with a total analytical acidity of 1 [124].

acetone are shown in Fig. 66; it is seen that the relationship in each case is nonlinear, and that, with the same solvent composition, $k_H/k_D \approx 7.7$ for all compositions. This corresponds to the true ratio of the enolization rates, determined by the different rates of removal of H^+ and D^+ atoms from carbon atoms. The variation of the bromination rate of "equilibrium" acetone (Curve III) i.e., acetone in which, as the result of prolonged preliminary exposure, the hydrogen isotope composition is the same as the isotope composition of the solvent, is quite different. The relationships observed in this and other cases are successfully explained by the peculiar variations of different acidic and basic forms with changes in the isotope composition of water. Fig. 67 shows these relationships for solutions with a total analytical acidity of 1.

§ 14. Kinetic Isotope Effects in Homogeneous Gaseous Reactions

The influence of isotopes on the rates of homogeneous gaseous reactions has been less thoroughly studied than the influence on the rates of reactions in solutions. Some types of reactions, such as intramolecular rearrangements of organic molecules, have been practically not studied at all, while others have not been studied systematically enough

With the development of chemical kinetics it is becoming increasingly clear that chain processes, active centers for which are neutral particles such as free atoms and mono- and biradicals [7], are predominant among chemical reactions in the gas phase. The high sensitivity of chain reactions to the action of small amounts of impurities, which may act as chain initiators or as inhibitors which terminate the chains, makes it practically impossible, for any elements except hydrogen, to attain the reproducibility of reaction rates necessary for determinations of kinetic isotope effects from different experiments with gases of different isotopic composition. Small separation coefficients have been extensively determined only recently, and therefore the available experimental material on isotope effects in thermal chain reactions is not very varied, complete, or reliable. It does not show sufficiently clearly the influence of isotopes on the separate characteristics of a chain reaction — chain initiation, branching, and termination. This gap has been partially filled by investigations of isotope effects in photochemical and radiochemical processes and work on the influence of isotopes on the reaction rates of artificially introduced free atoms and radicals. By introduction of such active particles in super-equilibrium concentrations the reaction scheme becomes simplified, and often the mechanism can be definitely established, which is highly important for comparisons with theory. We shall first consider the experimental data for this group of processes.

a) Simple reactions of atoms and radicals

A summary of the results up to 1938 is contained in Geib's review [173]. This review is entirely devoted to the influence of replacement of protium by deuterium in processes of this type. Subsequent work has not introduced any substantial corrections to the values given in Table 89, taken from this review.

The table compares the ratios of the observed rate constants with the ratios of the numbers of collisions, and the differences of the observed activation energies with the differences of the zero-point energies. It is clear from the comparisons that only in one case, for the recombination of atoms, can the isotope effect be completely explained by the higher rate of motion of H atoms (or H_2 molecules), which leads to a 1.41-fold increase in the number of collisions. It is known from the kinetic theory of gases that the number of collisions per second between molecules (or atoms) having molecular-kinetic diameters σ_1 and σ_2 is given by the equation

$$Z = 2\sqrt{2\pi}\cdot n_1 n_2 \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \sqrt{\frac{M_1 + M_2}{M_1 M_2} RT}, \tag{116}$$

where n_1 and n_2 are the numbers of molecules of types 1 and 2 in unit volume, M_1 and M_2 are their molecular weights. The expression under the radical is derived from the motion of molecules of types 1 and 2 with different mean velocities $\bar{C}_1 = \sqrt{\frac{8RT}{\pi M_1}}$ and $\bar{C}_2 = \sqrt{\frac{8RT}{\pi M_2}}$.

If one of the substances, e.g., substance 2, is replaced by an equimolar quantity of a substance 2*, isotopic with it, n_2 and σ_2 remain unchanged. Therefore, we may write, for the two isotopes,

$$\left.\begin{aligned} Z &= \text{const}\ \sqrt{\frac{M_1 + M_2}{M_1 M_2}} = \text{const}\ \sqrt{\mu^{-1}}, \\ Z^* &= \text{const}\ \sqrt{\frac{M_1 + M_2^*}{M_1 M_2^*}} = \text{const}\ \sqrt{\mu^{*-1}}. \end{aligned}\right\} \tag{117}$$

Hence, we have, for the ratio Z/Z^*

$$\frac{Z}{Z^*} = \sqrt{\frac{\mu^*}{\mu}} = \sqrt{\frac{(M_1 + M_2)\, M_1 M_2^*}{(M_1 + M_2^*)\, M_1 M_2}} = \sqrt{\frac{M_2^*(M_1 + M_2)}{M_2(M_1 + M_2^*)}} \tag{118}$$

In all cases when $M_1 \gg M_2$, the expression is simplified, and reduces to a simple ratio of the square roots of the molecular weights

$$\frac{Z}{Z^*} \approx \sqrt{\frac{M_2^*}{M_2}}. \tag{119}$$

In the replacement of H by D and of H_2 by D_2, $\sqrt{\frac{M_2^*}{M_2}} = 1.41$. This is the value assumed in the table. With

TABLE 89

Hydrogen Isotope Effects in Gaseous Reactions, after Geib

Reactions compared	T, °C	Ratio of rate constants k_1/k_2	Ratio of collisions Z_1/Z_2	Difference, in kcal/mole, of activation energies E_1-E_2	Difference, in kcal/mole, of zero point energies $E_{10}-E_{10}$	Literature
I. Reactions of H atoms						
$\frac{H+H+(M)}{D+D+(M)}$	20	1.4	1.41	0	0	[174]
$\frac{H+H_2}{D+D_2}$	630—710	1.85	1.41	0.52	1.8	[175]
$\frac{D+H_2O}{H+D_2O}$	183	~1.7	0.73	~0.75	3.6	[176]
$\frac{D+NH_3}{H+ND_3}$	260—400	3.2—2	0.73	1.5	5.6	[177]
$\frac{D+PH_3}{H+PD_3}$	420—620	1.04	1.4	0.6	4.3	[178]
II. Reactions of atoms of other elements with hydrogen and HCl						
$\frac{Na+ClH}{Na+ClD}$	238	1.33	1	0.35	1.2	[179]
$\frac{Cl+H_2}{Cl+HD}$	30	3.3	1.22	0.6	0.8	[180]
$\frac{Cl+H_2}{Cl+D_2}$	0 and 30	13.4 and 9.75	1.39	1.2	1.8	[181]
$\frac{Br+H_2}{Br+D_2}$	275—380	5.5—4.4	1.4	1.5	1.8	[182]
III. Reactions with molecular mechanisms						
$\frac{I_2+H_2}{I_2+D_2}$	425—500	2.45—2.1	1.41	0.75	1.8	[183]
$\frac{2HI}{2DI}$	430	1.53	1	0.6	0.93	[184]
$\frac{C_2H_4+H_2}{C_2H_4+D_2}$	530—570	2.5	1.4	0.95	1.8	[185]

the moderate accuracy of the calculations and determinations shown in the table there is no sense in taking into account deviations from this value, resulting from rejection of the fraction $\frac{M_1 + M_2}{M_1 + M_2^*}$. In some cases the observed difference of the activation energies is less than the difference of the zero-point energies, and therefore the isotope effects are less than the values calculated from the simplest model. Good agreement between calculated and experimental values is found for the reactions of chlorine and bromine atoms with hydrogen. The observed isotope effects are greatest in these cases, in particular, according to Rollefson [186], the value for $\frac{Cl + H_2}{Cl + D_2}$ at 0°C reaches 13.4. For most other reactions the isotope effect is considerably less – from 1.5 to 3.3. This indicates a considerable compensating effect of zero-point energy differences of intermediate complexes of different isotopic composition. The isotope effects in reactions of molecular hydrogen with chlorine atoms have been recently studied in detail; this work is of great theoretical interest.

Jones [187] has published the results of a very thorough study of the kinetic isotope effects in the reactions of hydrogen with chlorine, which to some extent formed a continuation of Rollefson's work [186]. The reaction was performed photochemically with hydrogen containing tritium in the form of HT molecules

The rate of the chain formation of HCl from ordinary hydrogen and chlorine is determined by the stage

$$1)\ H_2 + Cl \rightarrow HCl + H.$$

Therefore the change of the isotopic composition measured for the unreacted hydrogen, is determined by the ratio of the rate of Process 1) to the rate of the analogous reaction of chlorine atoms with mixed HT molecules. The latter, in turn, represents the sum of Reactions (2a) and (2b)

$$2a)\ HT + Cl \rightarrow H + TCl;$$
$$2b)\ HT + Cl \rightarrow T + HCl.$$

The isotopic composition of the hydrogen mass was used to calculate

$$\alpha = \frac{k_1}{k_2} = \frac{k_1}{k_{(2a)} + k_{(2b)}} = \log[(H_2)_0/(H_2)_f]/\log[(HT)_0/(HT)_f].$$

The subscripts 0 and f represent the initial contents of H_2 and HT and their contents at the cessation of the process. For four temperatures (−38, 0, 31.2, and 70.7°C) the following values were obtained for α: 4.48 ± 0.01, 3.72 ± 0.02; 3.33 ± 0.1 and 3.04 ± 0.01. The results are quite reliable. They show a very great discrepancy between the theoretically calculated and the experimentally determined isotope effects. Large deviations between theory and experiment are also found on comparing the theoretical values with the results obtained by Rollefson [186], van Meersche [188], and Italian workers [189]. As will be shown in Chapter VI, it is possible that discrepancies between theory and experiment are due to the unsuitable choice of a linear intermediate complex model for the calculations.

Numerous investigations have dealt with reactions of hydrogen and deuterium atoms with methane. The existing contradictions and obscure points have been largely eliminated by the latest paper by Majury and Steacie [190], which represents the conclusion of nearly 20 years of research by Steacie and his school [191].

Methyl radicals were obtained by photolysis of acetone, and their interaction with ordinary hydrogen and deuterium was studied at temperatures from 130 to 300°C. The ratios of the reaction rate constants at different temperatures can be determined directly from the experimental data. Data obtained for four radical reactions at 210° are given in Table 90. It is seen that the observed rate differences are considerable in replacement of H_2 by D_2 and small in replacement of CH_3 by CD_3. The magnitude of the effect in the first case, and its sign in the second, exclude the possibility of an explanation based on a change in the number of collisions. As in other cases, it is natural to associate the observed differences of the rate constants with differences of zero-point energies

It is easy to show that, for reactions between methyl radicals and molecular hydrogen, this explanation is in agreement with the observed value of the ratio (with change of Z_1/Z_2 taken into account). It is much more difficult to explain the decrease to 0.7 in the rate constants in passing from CD_3 to CH_3. This probably indicates the need to take into account the isotopic frequency displacement in the intermediate complex. A more detailed analysis is impossible, as the mechanism of the reaction between methyl and hydrogen is not clear. The Canadian authors [190] assume that the step which determines the rate of the whole process is

$$\left.\begin{array}{l} CH_3 + D_2 \rightarrow CH_3D + D; \\ CD_3 + H_2 \rightarrow CHD_3 + H \end{array}\right\} \qquad (120)$$

etc.

TABLE 90

Hydrogen Isotope Effects in the Reaction Rates of Methyl Radicals; after Majury and Steacie [190]

Reaction	T, °C	Ratio of rate constants
$\frac{CH_3 + H_2}{CH_3 + D_2}$	210	3.3
$\frac{CD_3 + H_2}{CD_3 + D_2}$	210	3.5
$\frac{CH_3 + H_2}{CD_3 + H_2}$	210	0.71
$\frac{CH_3 + D_2}{CD_3 + D_2}$	210	0.74

However, in view of the experimental conditions one cannot exclude the possibility of another interpretation, according to which the appearance of deuterium or protium in methane depends on isotopic exchange as postulated by Voevodsky

$$\left.\begin{array}{l} CH_3 + D_2 \rightarrow CH_2D + DH; \\ CD_3 + H_2 \rightarrow CD_2H + HD \end{array}\right\} \qquad (121)$$

etc.*

On the basis of the kinetic data obtained in the work, and of the data of earlier work by Wijnen and Steacie [193], Majury and Steacie found the activation energies given in Table 91.

To decrease the disagreement with the data of other authors [194], in view of possible experimental errors, the rounded off values of 9.7 for reactions of methyl radicals with H_2, and 11.3 for reactions of methyl radicals with D_2, are assumed. The difference between these two values of E is 1.6 kcal. The difference between the zero-point energies for H_2 and D_2 is 1.8 kcal. The agreement is good, but it was attained by a correction, the basis for which is doubtful, of the primary calculated results. There is also no complete certainty of the reality of the increase of E in the transition from methyl to ethyl radicals, especially as the opposite was found (Table 92) by Darwent and Roberts [195] for the activation energy of the reverse process – the removal of hydrogen from hydrocarbon molecules by deuterium atoms. Nevertheless, it is evident that E_1 and E_{-1}, according to the equation $E_1 = E_{-1} + Q$, should vary symbatically.

TABLE 91

Activation Energies for Reactions of Simple Monoradicals with Deuterium and Hydrogen

Reaction	Activation energy, kcal/mole	Notes
$CH_3 + H_2$	9.2±0.3	Determined experimentally
$CH_3 + D_2$	11.7±0.1	
$CD_3 + H_2$	10.2±0.2	
$CD_3 + D_2$	10.9±0.3	
$CH_3 + D_2$	11.7±0.5	Calculated from E_0 differences
$C_2H_5 + D_2$	13.3±0.5	
CH_3 (or CD_3) + H_2	9.7±0.6	Rounded off on the basis of literature data
CH_3 (or CD_3) + D_2	11.3±0.6	

It may be noted that, while contradictory data on the absolute values of the steric factors have been obtained, no one, in agreement with the theory, has observed any variations of these values with changes of isotopic composition.

b) Isotope effects in unbranched chain processes

As was pointed out at the beginning of this section, isotope effects in chain reactions have been studied relatively little. The available material shows that chain reactions do not differ significantly from nonchain reactions in the order of the observed values of α (and δ), which usually coincide with the values of α (and δ) of

TABLE 92

Activation Energies and Steric Factors for the Removal of Hydrogen Atoms from Hydrocarbons by Deuterium Atoms, after Darwent and Roberts [195]

Reaction	E, kcal/mole	P (steric factor)
Alkanes		
$C_2H_6 + D = C_2H_5 + HD$	9.0	0.6
$C_3H_8 + D = C_3H_7 + HD$	7.2	0.6
n-$C_4H_{10} + D = C_4H_9 + HD$	7.1	0.6
iso-$C_4H_{10} + D = C_4H_9 + HD$	6.3	0.6
Alkenes		
$C_3H_6 + D = C_3H_5 + HD$	5.0	0.1
sec.- $C_4H_8 + D = C_4H_7 + HD$	5.0	0.3

one of the stages of the chain process. The magnitude of the isotope effects decreases normally with increasing temperature and atomic weight.

Classical examples of unbranched chain reactions are: the addition of chlorine to hydrogen

$$H_2 + Cl_2 = 2HCl \qquad (122)$$

and the formation of phosgene from carbon monoxide and chlorine

$$CO + Cl_2 \rightarrow COCl_2. \qquad (123)$$

Both reactions can occur thermally, photochemically, and catalytically. The chain length ν is very great even at room temperature, and in absence of negative catalysts, in sufficiently large vessels, it can reach 10^5 for the formation of hydrogen chloride, and 10^3 for the formation of phosgene [196, 197].

Rollefson [186] determined the kinetic isotope effect for Reaction (122) by the following ingenious method, which eliminated the possibility of error due to discrepancies in the reaction conditions with the use of light and heavy hydrogen. Carbon monoxide was added to a mixture of hydrogen and chlorine, and the mixture was irradiated with white light which contained frequencies which activated the chlorine. The photochemical chain reactions represented by Equations (122) and (123) then occur simultaneously, atomic chlorine providing common active centers for both. The two reactions proceed in the following stages:

$$\left.\begin{array}{ll} Cl_2 + h\nu & \rightarrow \quad 2Cl \\ Cl + H_2 \rightarrow HCl + H & Cl + CO \rightarrow COCl \\ H + Cl_2 \rightarrow HCl + Cl & COCl + Cl_2 \rightarrow COCl_2 + Cl \\ Cl + H_2 \rightarrow HCl + H & Cl + CO \rightarrow COCl \\ \text{etc.} & \text{etc.}^{*} \end{array}\right\} \qquad (124)$$

The relative yields of HCl and $COCl_2$ in the chlorination of a mixture of hydrogen and carbon monoxide may be represented by the equation

$$\frac{\Delta[H_2] + \Delta[CO]}{\Delta[H_2]} = 1 + k\,[CO]/[H_2], \qquad (126)$$

---

*It must be pointed out that Steacie would not agree with this interpretation, since in the recent second edition of his monograph [192] he disputes Voevodsky's mechanism for deuterium exchange between radicals.

*The generation of active centers by light is attributed to wave lengths which induce dissociation. At longer wave lengths, light absorption may lead to formation of electronically excited molecules $Cl_2 + h\nu \rightarrow Cl_2^*$ (125), but the subsequent stage sequence is not affected by this [197].

where $\Delta[H_2]$ and $\Delta[CO]$ are the decreases of the H_2 and CO concentrations as the result of the reaction, and k is a constant. When the decreases of the hydrogen and carbon monoxide concentrations caused by chlorination are equal, i.e.,

$$\Delta[H_2] = \Delta[CO], \tag{127}$$

the left-hand side of Equation (126) is equal to two. Hence

$$1 + k[CO]/[H_2] = 2, \tag{126a}$$

$$k\frac{[CO]}{[H_2]} = 1 \text{ and } k = \frac{[H_2]}{[CO]} \tag{128}$$

But, at the same time,

$$k = \frac{k_{CO}}{k_{H_2}} \tag{128a}$$

Therefore the ratio of the hydrogen and carbon monoxide concentrations at which the hydrogen chloride yield is equal to twice the phosgene yield gives the ratio of the two rate constants. If these experiments are performed in the same conditions (T, p, light intensity) once with mixtures of H_2 and Cl_2, and once with mixtures of D_2 and Cl_2, and the values of the ratio $[H_2]/[CO]$ which satisfy the conditions of (128) are determined, the values $k_1 = \frac{k_{CO}}{k_{H_2}}$ and $k_2 = \frac{k_{CO}}{k_{D_2}}$ are found; i.e., the ratios of k_{H_2} and k_{D_2} to the same rate constant k_{CO}, which serves an auxiliary constant which vanishes from the final result and which does not cause any significant differences in the conditions of the experiments with D_2 and H_2. Division of one of these ratios by the other gives the required value

$$\alpha = \frac{k_{H_2}}{k_{D_2}}. \tag{129}$$

This value is very high at 0°C. To obtain equal consumption of H_2 and CO in chlorination, with light hydrogen in the mixture, the mixture must contain nearly four times as much carbon monoxide as hydrogen, $[CO]:[H_2] \approx 4$. With heavy hydrogen the same effect is obtained in mixtures with the proportions $[CO]:[D_2] \approx 0.25$.

Table 93 shows Rollefson's more accurate data for two temperatures. Rollefson's results are in qualitative agreement with the data obtained at the same time by the Farkas brothers in a study of the variation of the isotopic composition of a reacting gaseous mixture of deuterium-enriched hydrogen and chlorine [180].

TABLE 93

Kinetic Isotope Effect in the Reaction of Hydrogen with Chlorine, after Rollefson [186].

T, °C	k_{H_2}	k_{D_2}	k_{H_2}/k_{D_2}
0	3.7	0.275	13.4
32	16.6	1.70	9.75

The temperature course of the ratio corresponds to $\Delta E = 1630$ cal/mole, which is close to the zero-point energy difference $\Delta E_0 = 1800$ cal/mole.

There are good reasons for attributing the α found by Rollefson to the reactions

$$\left.\begin{array}{l} Cl + H_2 \rightarrow ClH + H \\ Cl + D_2 \rightarrow ClD + D \end{array}\right\} \tag{130}$$

The values of 2.1 to 3.7 found by the Farkas brothers for the ratio $\frac{\Delta P_H}{\Delta P_D} \cdot \frac{D_0}{H_0}$ at 30°C represent certain average values of α for the simultaneous occurrence of both reactions of Equation (130) and of the reaction

$$Cl + HD \begin{array}{l} \nearrow DCl + H \\ \searrow HCl + D \end{array}\Bigg\} \tag{131}$$

Since the value of E_{0HD} lies about half way between E_{0H_2} and E_{0D_2}, $\alpha_{H_2/HD}$ and α_{HD/D_2} at 32°C should be close to $\sqrt{\alpha_{H_2/D_2}} \approx 3$. It is probable that the lengths of the chains in the photochemical reactions of chlorine with molecular hydrogen of different composition, ν_{H_2}, ν_{HD}, etc., should be in the same ratio as the corresponding values of α, and it is to be expected that

$$\nu_{H_2} : \nu_{HD} : \nu_{D_2} \approx 9 : 3 : 1 \quad (\text{at } 30°C);$$
$$\nu_{H_2} : \nu_{HD} : \nu_{D_2} \approx 13 : 3.6 : 1 \quad (\text{at } 0°C).$$

Apparently no one has yet determined the values of ν for individual mixtures such as $H_2 + Cl_2$, $HD + Cl_2$, etc. In the paper by Jones [187], who studied the isotope effect in the exchange of protium with tritium, no determinations of the chain length are reported, and it is merely noted that the value found for R (see earlier, page 206) does not alter under the action of additions which lengthen the chain. All these results refer to the reactions of halogens in conditions in which a radical chain mechanism directly determines the observed rates. The isotope effects in reactions of the same type with combustion have different values. Thus, Cooley and Anderson [198], who studied the rates of flame propagation in mixtures of H_2 and D_2 with bromine, found 1.55-1.59 for the ratio $w_{H_2} : w_{D_2}$. This is only 10% higher than the ratio of the diffusion coefficients of H and D atoms. At the same time, the molar composition at which the rate of flame propagation is highest is the same for bromine – protium as for bromine – deuterium mixtures (43% Br_2). Consideration of these and certain other data led the authors to conclude that the observed isotope effect is in full agreement with the theory of combustion developed in the Soviet Union by Ya.B. Zeldovich and D.A. Frank-Kamenetsky [199] and in the United States by Tanford and Pease [200].

To complete the picture, we quote the data of Stranks [201], who determined the primary quantum yield for the photochemical decomposition of phosgene, which is the reverse of the reaction of phosgene formation mentioned at the beginning of this section. Both reactions pass through the same elementary stages. By a study of the photochemical isotopic exchange of carbon monoxide with phosgene Stranks showed that the quantum yield of the primary process $COCl_2 \rightarrow COCl + Cl$, which is practically unity, is the same both for $C^{12}OCl_2$ and $C^{14}OCl_2$ molecules.

Thus, there is no isotope effect in the primary step of photolysis, but it is large in the developing chain reaction in isothermal conditions, and is mainly determined by the difference of the zero-point energies of the rate-determining elementary step, while for combustion it is determined by the ratio of the diffusion coefficients of H and D.

c) Branched chain processes

Among branched chain reactions, the reactions studied from the aspects of interest to us have been the thermal and the radiochemical oxidation of hydrogen.

The mechanism of the oxidation of hydrogen by molecular oxygen is well understood. According to P.P. Semenov [196], Lewis and Elbe [202], and others, the initial centers are H atoms, and less often O atoms. Chain propagation occurs by alternation of reactions of H with O_2 (1) and of OH and O with H_2 (2 and 3). Chain branching, which determines the existence of sharp critical limits and other characteristics of the system, is associated with a combination of Reactions 3 and 1 (132). Chain growth is inseparable from branching and includes a stage with $E \approx 16$ kcal/mole, therefore the chain process 1-3 is impossible at room temperature. The essentials of the mechanism may be represented as follows

Stages of the thermal reaction

$$2H_2 + O_2 \rightarrow 2H_2O$$

	Q, kcal	E, kcal
Chain initiation		
$H_2 + \text{wall} \rightarrow \text{wall}\,H + H$	−50	50
Chain growth		
1) $H + O_2 \rightarrow OH + O$	−16	18
2) $OH + H_2 \rightarrow H_2O + H$	12	10
3) $O + H_2 \rightarrow OH + H$	−1	6

(132)

At low temperatures, addition reactions with negligible values of E may become dominant

$$\left.\begin{array}{l} 4)\ H + O_2 + M \rightarrow HO_2 + M \\ 5)\ O + O_2 + M \rightarrow O_3 + M \end{array}\right\} \qquad (132a)$$

These reactions terminate the chain, as the HO_2 radical and ozone are much less active than OH and O, and their participation in chain growth according to the equations

$$\left.\begin{array}{l} 6)\ HO_2 + H_2 \rightarrow H_2O_2 + H \\ 7)\ HO_2 + H_2O \rightarrow H_2O_2 + H \end{array}\right\} \qquad (132b)$$

may be neglected.

The oxidation of hydrogen is characterized by the existence of a limited flame combustion region, discovered in the experimental work of the Semenov school (A.V. Zagulin, P.Ya. Sadovnikov, and others) and of the Hinshelwood school [203]. The region has lower and upper pressure limits; it narrows from the low temperature side and broadens from the high temperature side; there is also a third limit, at which the second, upper flame region begins, which will not be discussed here. Outside the flame region the reaction was studied mainly with nonthermal activation. In the mercury-sensitized photochemical reaction the quantum yield was found to be two [204]. The quantum yield on direct activation by short ultraviolet radiation in the Schumann region is of the same order. Lind [205] obtained a yield of 3.9 H_2O molecules per each pair of ions formed by the action of α-particles. Marshall [206, 207] obtained a yield of the same order per pair of ions by the action of electrons.

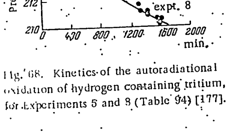


Fig. 68. Kinetics of the autoradiational oxidation of hydrogen containing tritium, for Experiments 5 and 8 (Table 94) [177].

All these results show that chain growth is impossible at low temperatures, which is to be expected in view of the considerable activation energy of stage 1. When the process occurs photochemically and radiochemically outside the flame region, the active centers are hydrogen atoms. There is no agreed opinion concerning the nature of the reactions of these atoms, but most authors attribute the principal role to Reaction 4.

A recent paper by Dorfman and Hemmer [208] reports a study of the isotope effect in the process for tritium. The reaction was activated by β-radiation from tritium. This radiation consists of a range of electrons of various energies with a maximum energy of 18000 ev [209] and an average energy of 5690 ev. In the experimental conditions used, practically all the electrons formed were absorbed within the gaseous volume. The reaction rate increases with partial pressure of tritium (Fig. 68), and rises somewhat if ordinary hydrogen is introduced into the system. In order to avoid complications caused by some self-retardation of the process, which is seen in Fig. 68 as appreciable deviations from linearity, the initial rates were compared. It may be noted that the partial pressures of tritium in Experiments 8 and 5 differed by a factor of more than 2 (73.8 and 32.4). The other experimental conditions are clear from Table 94.

The authors showed that the initial rate of the process is connected with the tritium concentration c_{T_2} and the mole fraction of protium m_H by the equation

TABLE 94

Reaction Rates of Tritium-Enriched Hydrogen with Oxygen Under the Influence of Electron Radiation from Tritium [208]

Expt. No.	Partial pressures of components, mm Hg			Material balance	$-\frac{dp}{dt}$, mm·min⁻¹·10³ at $t=0$	$k=\frac{w_0}{c_{T_2}(1+0.3\,m_H)}$, min⁻¹·10⁻⁴
	tritium	protium	oxygen	$p_{H_2O}/2\Delta p$		
7	104.4	7.4	69.4	0.94	6.16	1.16
1	95.8	16.9	115.5	0.97	6.57	1.31
2	92.6	10.5	218.3	0.97	5.03	1.06
8	73.8	4.4	138.0	0.96	4.53	1.21
10*	56.9	3.3	93.7	....	2.90	1.00*
9	45.2	127.3	99.9	....	3.26	1.18
4	42.2	16.4	106.8	0.98	2.62	1.14
11	39.8	195.9	68.9	....	2.80	1.13
6	37.5	72.2	90.2	....	2.94	1.31
5	32.4	82.1	103.0	....	2.12	1.08
3	30.2	18.5	184.0	0.96	2.24	1.30
					Average	1.19

* + 85.6 mm Krypton.

$$w_0 = kc_{T_2}(1 + bm_H). \qquad (133)$$

By this equation, the γ-yield per pair of ions, which can be represented by the ratio $\frac{w_0}{c_{T_2}}$, is

$$\gamma \approx \frac{w_0}{c_{T_2}} = k(1 + bm_H). \qquad (134)$$

Fig. 69 shows this relationship. The constant b is approximately 0.3. The average value of k is found to be $1.19 \cdot 10^{-4}$ min^{-1}. Calculation, from the results obtained, for the initial yields per pair of ions gives 3.2 molecules per pair of ions for pure tritium and 4.2 for pure protium. The last result is close to the value of 3.90 obtained by Lind for the reaction induced by α-particles. The most striking result of the very careful work of Dorfman and Hemmer, in our opinion, is the relatively low value of the isotope effect. Taking α to be the ratio of the initial ion yields, we have

$$\alpha = \frac{4.2}{3.2} = 1.31.$$

This is many times smaller than the effects produced by the difference in zero-point energies, which is more than 2500 cal/mole for T_2 and H_2

$$E_0^{H_2} - E_0^{T_2} \approx 2628 \text{ cal/mole} \qquad (135)$$

(see Table 19, Chapter I). Very surprisingly, α is even less than the ratio of the numbers of collisions, which in this instance is close to

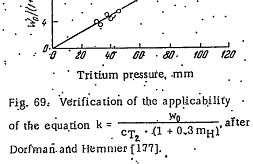


Fig. 69. Verification of the applicability of the equation $k = \frac{w_0}{c_{T_2} \cdot (1 + 0.3\,m_H)}$, after Dorfman and Hemmer [177].

$$\frac{Z_H}{Z_T} = \sqrt{\frac{m_T}{m_H}} = \sqrt{3} \approx 1.75.$$

On the other hand; for any process involving particles other than pure hydrogen, such as OH, HO_2, etc., the value of α, 1.30 is considerably greater than the ratio of the two values of Z. The data are inadequate for a final selection of the mechanism of the determining step, but the authors are inclined to consider that this step is the addition of hydrogen atoms to oxygen atoms.

$$\left.\begin{array}{l} T + O_2 + M \rightarrow TO_2 + M; \\ H + O_2 + M \rightarrow HO_2 + M. \end{array}\right\} \qquad (136)$$

The simplest explanation of the decrease of α in a reaction of this kind from 1.75 to 1.30 involves taking into account diffusion of atoms to the walls of the vessel, where free atoms are captured and recombined. This process plays an important part in the kinetics of hydrogen oxidation, and, according to Melville [210] it accounts for the practical equality of the oxidation rates of H and D atoms, obtained photochemically, at low temperatures. Since, under equal conditions, tritium diffuses much more slowly than protium, the recombination of its atoms should also occur more slowly, while their quasi-stationary concentration should be higher than for protium. The influence of this factor should diminish with increase of total pressure. According to Melville, this superposition of two effects, caused by mass and mobility differences, results in complete compensation only at low temperatures, when the chains cannot grow and the observed rate is determined by the reaction

$$H + O_2 + M \rightarrow HO_2 + M.$$

or, respectively,

$$D + O_2 + M \rightarrow DO_2 + M$$

At higher temperatures, with considerable chain lengths, the oxidation rates of H and D are sharply increased and appreciable differences appear between them.

The situation is entirely different at the boundaries of the flame region. According to Frost and Hinshelwood *et al.* [211] the lower boundary of thermal ignition is the same both for H_2 and D_2. Since the critical conditions are determined mainly by the probability of chain branching, the latter should be the same for H_2 and D_2. This may be an indication of the nonparticipation of hydrogen in the primary branching step. On the other hand, the upper limit is higher for D_2 than for H_2. This is in agreement with the usual concepts, according to Hinshelwood's theory, of deactivation on collision with participation of hydrogen. Thus, isotope effects are different for different conditions of the chain oxidation reaction, and variations in the magnitude of these effects correspond to changes in the mechanism.

d) Nonchain reactions with a molecular mechanism

From the first investigations of the chain mechanism of ordinary thermal reactions, there has been an intrusion, not yet ended, of radical and chain mechanisms into the field of ordinary molecular reactions. For example, many reactions of monomolecular decomposition of organic molecules, for long regarded as typical simple reactions, have proved to have a chain mechanism. Even in the reaction of iodine with hydrogen and the reverse, decomposition of hydrogen iodide the temperature variations of the rate constant have shown anomalies which can hardly be accounted for by the statistical theory [212, 213] of bimolecular reactions. Nevertheless, from the early work of Bodenstein [214], for 60 years these processes have been regarded as the classic examples of simple bimolecular reactions, used for verification of all the quantitative theory of absolute reaction rates. Recently Benson and Srinivasan [215] have obtained experimental results which provide serious evidence for the superposition, above 600°K, of an atomic chain process on the molecular reaction. The mechanism postulated for the chain process is analogous to that assumed for $H_2 + Cl_2$ and $H_2 + Br_2$; the possibility of which in the reaction of hydrogen and iodine was considered by Lewis and Rideal as long ago as 1926 [216]:

$$\left.\begin{array}{l} I_2 + M \rightleftharpoons 2I + M \; -35.6 \text{ kcal}; \\ I + H_2 \rightleftharpoons HI + H \; -32.8 \text{ kcal}; \\ H + I_2 \rightleftharpoons HI + I \; +35.5 \text{ kcal}. \end{array}\right\} \qquad (137)$$

Recently N.N. Semenov [7], on the basis of general theoretical concepts of the probabilities of intermediate complexes of different configurations, postulated another, more likely scheme for initiation of the reaction

$$IH + HI \rightarrow H_2 + 2I. \qquad (138)$$

It is therefore not clear whether combination and decomposition according to the equation

$$H_2 + I_2 \rightleftharpoons 2HI \qquad (139)$$

actually occur, and with what real process or step the kinetic isotope effect given in Table 89 is associated.

Such complications are very typical of the modern state of gaseous reaction kinetics, and therefore it is not easy to choose reliable illustrations of the magnitude of kinetic isotope effects in simple molecular processes. We will confine ourselves to one example, the molecular mechanism of which follows with some degree of certainty from measurements of the separation coefficients. This is the decomposition of ethyl bromide, the redistribution of C^{13} isotope in the course of this reaction was studied by Friedman, Bernstein and Gunning [217]. The aggregate process is represented by the equation

$$C_2H_5Br \rightarrow C_2H_4 + HBr. \qquad (140)$$

Because of the presence of two isotopes C^{12} and C^{13}, which in the following equations are designated by C and $\overset{*}{C}$ respectively, three parallel reactions occur:

$$\left.\begin{array}{l} 1)\; CH_3CH_2Br \rightarrow CH_2{=}CH_2 + HBr \quad k_1, \\ 2)\; CH_3\overset{*}{C}H_2Br \rightarrow CH_2{=}\overset{*}{C}H_2 + HBr \quad k_2, \\ 3)\; \overset{*}{C}H_3CH_2Br \rightarrow \overset{*}{C}H_2{=}CH_2 + HBr \quad k_3. \end{array}\right\} \qquad (141)$$

It is natural to assume that the mechanism of these reactions is of the same type, since replacement of C^{12} by C^{13} cannot affect it. The kinetics of this reaction in the gas phase and in presence of catalysts has been studied repeatedly, without isotopic determinations, over the last 25 years [218, 219], in particular by Daniels and his associates [220], who postulated a radical mechanism with primary formation of ethyl radicals

$$\left.\begin{array}{l} 1)\; C_2H_5Br + \text{Wall} \rightarrow C_2H_5 \cdot \text{Wall} + Br; \\ 2)\; C_2H_5Br + Br \rightarrow C_2H_4Br + HBr; \\ 3)\; C_2H_4Br \rightarrow C_2H_4 + Br; \\ 4)\; C_2H_4Br + C_2H_5 \rightarrow C_2H_4 + C_2H_5Br; \\ 5)\; Br + Br \rightarrow Br_2. \end{array}\right\} \qquad (142)$$

and bromine atoms. The latter react with ethyl bromide to give C_2H_4Br, which is then, by Reaction 3), converted into ethylene [221, 222], giving rise to a new atom of bromine, etc. The chain-terminating stages to be considered are the recombination of bromine with C_2H_4Br and Reactions 4) and 5). The last of these publications gave the results of experiments on the isotopic exchange of ethyl bromide with hydrogen bromide tagged in the bromine, and deuterium bromide. The activation energy of the first process was 31.5 kcal, and of the second, 40 ± 4 kcal. All 5 atoms in ethyl bromide exchange with deuterium bromide. The authors consider that these results and other qualitative observations constitute proof of the chain mechanism of the exchange, which has stages in common with the thermal decomposition of EtBr.

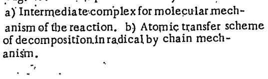


Fig. 70. Decomposition of ethyl bromide. a) Intermediate complex for molecular mechanism of the reaction. b) Atomic transfer scheme of decomposition in radical by chain mechanism.

Arguments against the Daniels radical-chain mechanism are reported by studies of the products of pyrolysis in the presence of toluene, in which no dibenzyl as a side product was detected [223]. It was therefore concluded that the decomposition occurs by intramolecular splitting of the saturated compound, with a transition compound of a four-membered ring structure, as shown in Fig. 70,a.

Fig. 70,b shows the most difficult first step of the chain scheme (wall omitted). According to Scheme b, in the rupture of the C – Br bond, by the Bigeleisen – Slater approximation, the minimum ratio of the rate constants $\frac{k_1}{k_2}$ for the rupture of C^{12} – Br and C^{13} – Br bonds, which expresses the magnitude of the primary intramolecular isotope effect, should be 1.036. The magnitude of the isotope effect for the cleavage of the intramolecular tetraatomic complex can be approximately calculated by means of the method developed by Bigeleisen and Wolfsberg [224] for three centers, with the corrections introduced as the result of Slater's critical comments [225]. This calculation gives α_1 = 1.003-1.036. Thus:

$$\left.\begin{aligned} \alpha_{\min \mathrm{I}} &= 1.003; \\ \alpha_{\min \mathrm{II}} &= 1.036; \end{aligned}\right\} \qquad (143)$$

$\delta = \alpha - 1$ shows a 12-fold difference for the two schemes, which makes the use of determinations of the separation coefficients in decomposition promising for determining the mechanism. Unfortunately, the ratio k_1/k_2 cannot be determined directly because the decomposition products according to Equations (141,2) and (141,3) are identical. Therefore the directly determined separation coefficients are the results of summation with introduction of the corresponding coefficients (k_1/k_2) and (k_1/k_3). It can be proved theoretically that α coincides with the separation coefficient at infinitely low decomposition S_0. Assuming $k_2 \approx k_3$, the authors determine α from the approximate formula

$$\alpha = S_0 = \frac{2k_1}{k_2 + k_3} = \frac{\ln(1 - f)}{\ln(1 - f/S)}, \qquad (144)$$

where f is the fraction of ethyl bromide decomposed and S is the separation factor determined at the final decomposition stage. When f < 0.1 a still simpler equation can be used

$$\delta = \delta' (1 + f/2), \qquad (145)$$

where

$$\delta = \alpha - 1$$

and

$$\delta' = S - 1.$$

This was used to determine α for various temperatures. The results are given in Table 95, which illustrates the reliability of results obtainable at the modern level of mass spectrometry.

Fig. 71 shows that α falls linearly with increasing temperature according to the equation

$$\alpha = 1 + \delta_0 = 1.0094 - 2.8 \cdot 10^{-5} (T - 350), \qquad (145)$$

where T is centigrade temperature. Not being able to determine directly the shares of the primary and secondary intramolecular effects in the separation, the authors estimated their probable values and accurately determined the maximum possible values of the primary isotope effect. The values found for k_1/k_2 for different temperatures are given in Fig. 72. At 400°C $k_1/k_{2\max} = 1.0159 \pm 0.0012$. The corresponding value of δ_1 (0.0159) is less than half of the minimum theoretical value for exchange with dissociation into a radical and an atom ($\delta_{1\text{theor}} = 0.036$). This is a serious argument against the chain mechanism (142). The positive conclusion concerning the molecular mechanism with participation of four atoms is less convincing, as at present the methods for calculating δ_1 for reactions of this type are not sufficiently well developed, and the calculation provides very extensive possibilities for variations of δ. Therefore the possibility of some, perhaps a third, mechanism cannot be excluded. Despite this defect, the above example demonstrates the applicability of the statistical theory to the decomposition of gaseous molecules, and the possibility, in principle, of its use to discriminate between a radical chain and a molecular mechanism. The results obtained are very typical both in the magnitude of the isotope corrections, and in the value of the results. The important fact is that the same theory is applicable and gives quantitative results for such dissimilar conditions as the reactions of free neutral gaseous molecules and the reactions of solvated and ionized particles in electrolyte solutions.

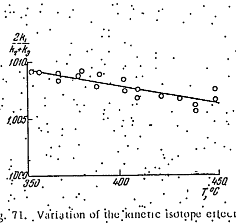


Fig. 71. Variation of the kinetic isotope effect α with the temperature in the decomposition of ethyl bromide [217].

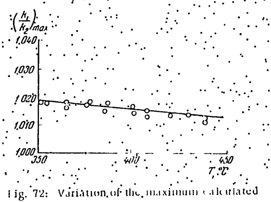


Fig. 72: Variation of the maximum calculated values of the primary isotope effect with the temperature, in the decomposition of ethyl bromide [217]

TABLE 95

Experimental Data on the Kinetic Coefficients of Isotopic Separation of C^{12}/C^{13} in the Decomposition of Ethyl Bromide [217]

T, °C ($\pm 3 \cdot 10^{-3}$)	f ($\pm 1 \cdot 10^{-4}$)	S ($\pm 5 \cdot 10^{-4}$)	$S_0 = \alpha$ ($\pm 5 \cdot 10^{-4}$)	T, °C ($\pm 3 \cdot 10^{-4}$)	f ($\pm 3 \cdot 10^{-4}$)	S ($\pm 5 \cdot 10^{-4}$)	$S_0 = \alpha$ ($\pm 5 \cdot 10^{-4}$)
351	0.053	1.0088_5	1.0091	402	0.061	1.0082_5	1.0085
355	0.050	1.0088	1.0090_5	403	0.059	1.0072	1.0074_5
366	0.056	1.0087_5	1.0090	410	0.056	1.0066_5	1.0068_5
366	0.057	1.0080	1.0082_5	410	0.057	1.0073_5	1.0076
377	0.062	1.0086	1.0088_5	423	0.054	1.0068	1.0070
379	0.057	1.0089_5	1.0092_5	433	0.063	1.0066	1.0068
387	0.050	1.0075_5	1.0077_5	442	0.089	1.0054	1.0056_5
389	0.059	1.0087	1.0090	442	0.078	1.0060	1.0062_5
—	—	—	—	453	0.123	1.0071_5	1.0076_5
—	—	—	—	453	0.071	1.0063_5	1.0066

§ 15. New Trends in Investigations of Hydrogen Isotope Effects

In § 6 we drew attention to the contrast between the rapid accumulation of experimental data on kinetic isotope effects for hydrogen in the 1930's, when these effects were at the center of attention of research workers in isotope chemistry, and the slow progress in this field in the 1940's.

The great advances made in interpretations of the mechanisms of organic reactions by means of detailed investigations of α and δ for other elements have, in the last few years, led to revived interest in kinetic isotope effects for hydrogen. However, the work of the last few years is not a simple continuation of the researches of the 1930's. On the basis of a more perfect theory and with the use of more accurate experimental methods, more complex and more difficult problems are being attacked and solved. The possibility of a systematic comparison of the behavior of deuterium and tritium plays an important part in this. These investigations embrace a wide range of problems. Thus, many investigations have dealt with distinctions between processes which anclude rupture and formation of C−H bonds at the determining step, and reactions in which bonds with hydrogen are not involved in the determining step. To judge by the magnitude of the isotope effects, the latter class includes the oxidation of isopropyl alcohol [226] and the displacement of bromine in the reaction of isopropyl bromide with alcoholates [227]. A detailed analysis of the problem was apparently made by Melander [228] in a paper which is known to us only through abstracts. A series of investigations have dealt with the role of hyperconjugation and other electronic effects in the reactions of carbonium ions. Of these, we will cite only the work of Lewis and Boozer [229]. These studies, like many others, are to a great extent associated with the development and verification of Ingold's theory of nucleophilic and electrophilic mechanisms. Wiberg [140] has published a full review.

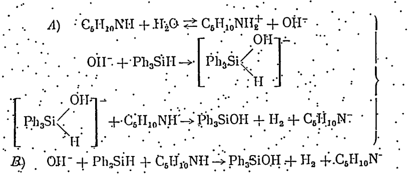
We shall consider in somewhat greater detail an interesting group of investigations of the mechanism of the removal of hydrogen from alkyl and aryl silanes by the action of alkalies. Reactions of this type may be represented by the general equation

$$R_3SiH + OH^- + HS \rightarrow R_3SiOH + H_2 + S^- \qquad (146)$$

This is a peculiar substitution of hydrogen in Si−H by hydroxyl with participation of solvent molecules HS. In solutions containing water, OH^- and S^- coincide, and Equation (146) can be written as

$$R_3SiH + H_2O \rightarrow R_3SiOH + H_2 \qquad (147)$$

The rate of the process, which has been the subject of numerous investigations in recent years, can be conveniently followed by the evolution of molecular hydrogen. The substitution mechanism is not entirely clear, but there are serious grounds for considering it to be nucleophilic with respect to the action on Si, proceeding either by bimolecular substitution (S_N2) with inversion of the tetrahedron, or by monomolecular ionization (S_N1). On the basis of the kinetic characteristics of the process for the particular case of the reaction between triphenylsilane and moist piperidine, Gilman et al. [230] represented these two mechanisms as follows:



$$\left.\begin{aligned} A)\quad & C_5H_{10}NH + H_2O \rightleftarrows C_5H_{10}NH_2^+ + OH^- \\ & OH^- + Ph_3SiH \rightarrow \left[Ph_3Si\begin{smallmatrix} OH \\ H \end{smallmatrix} \right]^- \\ & \left[Ph_3Si\begin{smallmatrix} OH \\ H \end{smallmatrix} \right]^- + C_5H_{10}NH \rightarrow Ph_3SiOH + H_2 + C_5H_{10}N^- \end{aligned}\right\} \qquad (148)$$

$$B)\quad OH^- + Ph_3SiH + C_5H_{10}NH \rightarrow Ph_3SiOH + H_2 + C_5H_{10}N^- \qquad (149)$$

To decide the choice between A) and B), comparative experiments with ordinary and deuterosilane Ph_3SiD were carried out; however, contrary to expectations, deuterosilane reacted six times as rapidly as the ordinary silane, and this cast doubts on all the results of the preceding investigations. This unexpected result led Kaplan and Wilzbach [231] to verify the conclusions by determining the isotope effect from the separation coefficients with the use of tritium instead of deuterium. Instead of an intensification of the effect, they observed an effect of normal sign, and concluded that the results found by Gilman et al. are erroneous because of the different conditions which resulted when the reaction rates for isotopic molecules were compared in independent experiments.

In the next investigation, Kaplan and Wilzbach [232] made a very careful study of hydrogen isotope effects in mixtures of Ph_3SiH with Ph_3SiD and Ph_3SiT, and also mixtures of $(n\text{-}C_3H_7)_3SiH$ and $(n\text{-}C_3H_7)_3SiT$.

Table 96 gives the results of experiments with moist piperidine and caustic potash in aqueous ethanol.

With mechanism A), α should be close to unity, as in order to explain the observed reaction kinetics in this case it must be assumed that the determining step is the formation of the addition complex $[R_3SiOH \cdot H]^-$, and in this step no bonds including hydrogen atoms are formed or broken. We may note that in this complex there are 10 electrons around the silicon atom, which is quinquevalent!

TABLE 96

Separation Coefficients of Hydrogen Isotopes in Reactions of Silanes with OH^- [232]

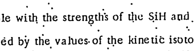
T, °C	Compared reactions	Solvent — reagent	$\alpha = \frac{k_{SiH}}{k_{SiX}}$
25	Ph_3SiH/Ph_3SiD	Piperidine — water	1.152±0.004
0	Ph_3SiH/Ph_3SiT		1.288±0.008
25	Ph_3SiH/Ph_3SiT		1.257±0.003
25	Ph_3SiH/Ph_3SiT	$C_2H_5OH—H_2O—KOH$	1.400±0.006
25	$(n\text{-}C_3H_7)_3SiH/(n\text{-}C_3H_7)_3SiT$		1.490±0.011

TABLE 97

Isotope Effect on Substituting a Tritium for a Protium Solvent [232]

T, °C	Silane	Solvent	k_{SiH}/k_{SiT}
0	$(Ph)_3SiH$	Piperidine — water	3.32±0.01
25	$(Ph)_3SiH$		3.05±0.02
25	$(Ph)_3SiD$		3.00±0.02
25	$(Ph)_3SiH$	$C_2H_5OH—H_2O—KOH$	6.96±0.06
25	$(Ph)_3SiD$		7.25±0.05
25	$(n\text{-}C_3H_7)_3SiH$		3.98±0.02

With mechanism B) which we do not consider in its separate stages, bonds including hydrogen are broken and formed, and α should be large. The experimental value of α was found to be considerably lower than the value expected from the zero-point energies and reduced masses. We have already met other examples of numerical discrepancies between theory and experiment in processes involving intermediate complexes of complicated structure. The authors used interesting comparisons in an attempt to explain the lower value of α, and concluded that the main reason for the lowering of α is strong interaction of the silane with the solvent. In consequence the silane hydrogen in the intermediate complex is linked to the solvent hydrogen by hydrogen bonds



$$(HO)^- \cdots \underset{Ph}{\overset{Ph\quad Ph}{Si}} - H \cdots H - S,$$

the strength of which is comparable with the strengths of the SiH and SH bonds which are broken in the process.

This explanation is confirmed by the values of the kinetic isotope effects observed when tritium is introduced into the solvent. The results of these experiments, given in Table 97, indicate that changes in the isotopic composition of the solvent influence the rate of the process more strongly than does substitution of H by T in the silane molecule.

The fact that the value of α changes by more than a factor of two when one solvent is replaced by the other, is also very instructive. It is a sign of the active participation of the solvent in the formation of the intermediate complex in the determining step, and is quite incompatible with mechanism A).

Further investigations in this direction might make it possible to clarify further the nature of mechanism B) and the participation of the solvent in the reaction. The possibility of intermediate formation of R_3Si^+ ions, the analogs of carbonium ions, can be regarded as excluded for this group of reactions.

§ 11. The Significance of Isotope Effects in Chemical Kinetics

We conclude this chapter on kinetic isotope effects with an attempt to assess their significance in chemical kinetics, and their theoretical level. The achievements of the statistical theory of isotope effects have opened a new and promising route for investigation of the nature of intermediate complexes formed in the rate-determining stages of chemical reactions. By this route it is possible in principle to obtain direct information on the nature of the bonds which join the original molecules in an intermediate complex, and on the nature of the bonds which are broken in the rate-determining step. Thus, intermediate complexes, which for 15 years remained elusive, can now be studied by direct experimental methods.

The great majority of the experimental data obtained before the emergence of the new theories was concerned with hydrogen isotopes. Because of the high values of their isotope effects there was no need for special precision in the theory and in the methods for determination of the separation coefficients α and δ from experimental data. As the theory was perfected it became necessary to make exact quantitative studies of kinetic isotope effects for the heavier elements C, N, and O, which form the skeleton of an organic molecule. This demanded more precise methods by which small differences of isotopic composition could be reliably measured, and improved methods for calculation of α and δ from the results of such measurements.

The first problem can be successfully solved by modern mass spectrometry and radiometry. To solve the second problem, many investigators have carried out extensive analyses of the relationships between the experimentally observed changes of the isotopic composition of the original substances and the reaction products, and the separation coefficients α and δ. These analyses have resulted in rational methods for experimental determination of α and δ, and considerable improvements in the methods for the theoretical treatment of the primary experimental data. This created favorable conditions for systematic investigations of the kinetic isotope effects for the above-mentioned elements, and increased the number of experimental studies devoted to various individual processes and groups of reactions. The new stage in the study of kinetic isotope effects has only just started, and it is too early to assess its results; but the examples given above clearly demonstrate the promising nature of this trend and the value of the results obtained. The imperfections of the statistical theory in relation to processes, the determining step of which cannot be schematically reduced to the cleavage or formation on one bond, have also been revealed. In such cases the Slater and Bigeleisen formulas are not directly applicable; and the theory becomes only roughly approximate. It is therefore necessary to develop the theory further, on the basis of the results obtained for more complex reactions and of spectroscopic data for complex molecules.

LITERATURE CITED

[1] B.H. Billings, W.J. Hitchcock and M. Zelikoff, J. Chem. Phys. 21, 1762 (1953).

[2] Progr. Phys. Sci. 55, 315 (1955).

[3] D.A. Frank-Kamenetsky, Diffusion and Heat-Transfer in Chemical Kinetics, Moscow, Acad. Sci. USSR Press (1947). V.G. Levich, Physicochemical Hydromechanics, Moscow, Acad. Sci. USSR Press (1952); G.K. Boreskov, Problems of Kinetics and Catalysis 6, 404 (1949).

[4] S. Glasstone, K. Laidler and H. Eyring, Theory of Rate Processes, Moscow, Foreign Lit. Press (1948).

[5] R. Marcelin, Ann. phys. 3, 158 (1915).

[6] H. Eyring and M. Polanyi, Z. Phys. Chem. B12, 279 (1931); H. Eyring, Chem. Rev. 10, 103 (1932); Trans. Far. Soc. 34, 3 (1938); J. Chem. Phys. 3, 107 (1935); M.G. Evans and M. Polanyi, Trans. Far. Soc. 31, 875 (1935).

[7] N.N. Semenov, Some Problems of Chemical Kinetics and Reactivity; Moscow, Acad. Sci. USSR Press (1954).

[8] M.I. Temkin, J. Phys. Chem. 11, 169 (1938).

[9] G.E. Kimball, J. Chem. Phys. 6, 447 (1938).

[10] H.M. Rosenstock, M. Wallenstein, A.L. Wahrhaftig and H. Eyring, Proc. Nat. Acad. Sci. 38, 667 (1952).

[11] F.A. Matsen, J. Chem. Phys. 22, 165 (1954).

[12] J.C. Giddings and H. Eyring, ibid. 22, 538 (1954).

[13] R.S. Barker and H. Eyring, J. Chem. Phys. 22, 1182 (1954).

[14] N.B. Slater, Proc. Roy. Soc. A194, 112 (1948).

[15] E. Wigner, Z. phys. Chem. B19, 203 (1932).

[16] J. Bigeleisen, J. Chem. Phys. 17, 675 (1949).

[17] J. Bigeleisen and M. Mayer, J. Chem. Phys. 15, 261 (1947).

[18] J. Bigeleisen, J. Phys. Chem. 56, 823 (1952).

[19] J. Lindsay, A.N. Bourns and H. Thode, Canad. J. Chem. 29, 192 (1951).

[20] F.W. Stacey, J. Lindsay and A.N. Bourns, Canad. J. Chem. 30, 135 (1952).

[21] J. Bigeleisen, Canad. J. Chem. 30, 443 (1952).

[22] L. Friedman and J. Bigeleisen, J. Chem. Phys. 18, 1325 (1950).

[23] A.A. Bothner-By and J. Bigeleisen, J. Chem. Phys. 19, 755 (1951).

[24] L. Landau and V. Lifshits, Quantum Mechanics, Pt. I (Moscow–Leningrad, 1948), p. 490. D.I. Blokhintsev, Principles of Quantum Mechanics, 2nd ed. (Moscow, 1949); p. 473.

[25] J. Bigeleisen and L. Friedman, J. Chem. Phys. 17, 998 (1949).

[26] P. Yankwich, E.C. Stivers and R. Nystrom, J. Chem. Phys. 20, 344 (1952).

[27] P. Yankwich and M. Calvin, J. Chem. Phys. 17, 109 (1949).

[28] A. Roe and M. Hellman, J. Chem. Phys. 19, 660 (1951).

[29] A. Fry and M. Calvin, J. Phys. Chem. 56, 901 (1952).

[30] A. Fry and M. Calvin, J. Phys. Chem. 56, 897 (1952).

[31] J. Lindsay, D.E. McElcheran and H. Thode, J. Chem. Phys. 17, 589 (1949).

[32] W.H. Stevens, J.M. Pepper and M. Lounsbury, J. Chem. Phys. 19, 760 (1952).

[33] K.S. Pitzer, J. Chem. Phys. 17, 1341 (1949).

[34] J. Bigeleisen, J. Chem. Phys. 17, 425 (1949).

[35] H. Eyring and W. Cagle, J. Phys. Chem. 56, 889 (1952).

[36] W. Janke and F. Emde, Tables of Functions with Formulas and Curves, Moscow, State Tech. Press (1948).

[37] G. Ropp and V. Raaen, J. Phys. Chem. 22, 1223 (1954).

[38] J. Schmidt, A. Myerson and F. Daniels, J. Phys. Chem. 56, 917 (1952).

[39] A.N. Frumkin, V.S. Bagotsky, Z.A. Iofa and B.N. Kabanov, Kinetics of Electrode Processes, Moscow, Moscow State University Press (1952).

[40] G. Ropp, A.J. Weinberger and O.K. Neville, J. Am. Chem. Soc. 73, 5573 (1952)

[41] J. Bigeleisen, Science 110, 14 (1949).

[42] G. Ropp, Nucleonics 10, 22 (1952).

[43] R.W. Attree and W.H. Stevens, Canad. J. Res. B27, 807 (1949), J. Chem. Phys. 18, 574 (1950).

[44] F. Brown and A. Holland, Canad. J. Chem. 30, 438 (1952).

[45] G. Ropp and V. Raaen, J. Chem. Phys. 20, 1823 (1952).

[46] V. Raaen and G. Ropp, Ann. Chem. 25, 478 (1953), [37].

[47] G.P. Miklukhin, Doctorate Dissertation, Inst. Phys. Chem., Acad. Sci. Ukrainian SSR (Kiev, 1954)

[48] L.P. Hammett, Physical Organic Chemistry (New York, 1940)

[49] A.I. Brodsky and M.A. Vysotskaya, Proc. Acad. Sci. USSR 101, 869 (1955).

[50] A.I. Brodsky and L.V. Sulima, Proc. Acad. Sci. USSR 92, 589 (1953); L.V. Sulima, "Investigation of the Mechanism of Hydrogen and Oxygen Exchange in Ammonium Salts and the Acids of Phosphorus, and Tautomerism of the Latter," Dissertation, L.V. Pisarzhevsky Inst. Phys. Chem. (Kiev, 1954); V.V. Fesenko and I.P. Gragerov, Proc. Acad. Sci. USSR 101, 695 (1955).

[51] H. Fredenhagen and K.F. Bonhoeffer, Z. phys. Chem. A181, 379 (1938).

[52] K. Geib, Handbuch der Katalyse, 3, 36 (1943).

[53] M. Dole, D.F.P. Rudd, G. Muchow and C. Comto, J. Chem. Phys. 20, 961 (1952).

[54] F.R.S. Winter and H.V.A. Briscoe, J. Am. Chem. Soc. 73, 3055 (1951).

[55] A.E. Cahill and H. Taube, J. Am. Chem. Soc. 74, 2312 (1952).

[56] P. Giguere, J. Chem. Phys. 18, 88 (1950).

[57] W. Penny and G. Sutherland, J. Chem. Phys. 2, 492 (1934); N.W. Luft, J. Chem. Phys. 21, 179 (1953).

[58] J. Massey and D. Bianko, J. Chem. Phys. 22, 442 (1954).

[59] S.Z. Roginsky, Problems of Kinetics and Catalysis 8, 195 (1955).

[60] F. Haber and R. Willstätter, Ber. 64, 2844 (1931); F. Haber and J. Weiss, Proc. Roy. Soc. A147, 332 (1934).

[61] J. Weiss, Adv. Catal. 4, 343 (1952).

[62] J. Baxendale, Adv. Catal. 4, 31 (1952).

[63] J. Schmidt and F. Daniels, J. Am. Chem. Soc. 75, 3564 (1953).

[64] A. Downes, Austral. J. Scien. Res. 5, 521 (1952).

[65] L. Kelner, Proc. Roy. Soc. A274, 456 (1941).

[66] F. Daniels, Chemical Kinetics (New York, 1938).

[67] I. Jungers and H. Taylor, J. Am. Chem. Soc. 57, 679 (1935).

[68] M.I. Temkin and V.I. Pyzhov, J. Phys. Chem. 13, 851 (1939).

[69] M.I. Temkin and S.L. Kiperman, J. Phys. Chem. 21, 927 (1947).

[70] M.I. Temkin, J. Phys. Chem. 24, 1312 (1950).

[71] A. Nielsen, Adv. Catal. 5, 1 (1953).

[72] G. Joris and H. Taylor, J. Chem. Phys. 7, 893 (1939).

[73] J. Kummer and P. Emmett, J. Chem. Phys. 19, 289 (1951).

[74] G.P. McGeer and H. Taylor, J. Am. Chem. Soc. 73, 2743 (1952).

[75] A.V. Romanushkina and S.L. Kiperman, J. Phys. Chem. 27, 1181 (1953).

[76] S.Z. Roginsky, Catalysis and Adsorption at Heterogeneous Surfaces, Moscow, Acad. Sci. USSR Press (1948).

[77] I. Singleton, B. Roberts and E. Winter, Trans. Far. Soc. 47, 1318 (1951).

[78] S. Kemball, Proc. Roy. Soc. A214, 413 (1952); Trans. Far. Soc. 48, 254 (1952).

[79] S.Z. Roginsky and V.S. Rozing, Annals State Univ. Leningrad, No. 38, 67 (1939).

[80] O.V. Krylov, Dissertation, Inst. Phys. Chem. Acad. Sci. USSR (1950).

[81] O.V. Krylov and S.Z. Roginsky, Proc. Acad. Sci. USSR 88, 293 (1953); S.Yu. Elovich and V.S. Rozing, Problems of Kinetics and Catalysis 3, 449 (1937).

[82] H.W. Melville, J. Chem. Soc. 1243 (1931).

[83] H.W. Melville, J. Chem. Soc. 804 (1934).

[84] F. Tucholski, Z. phys. Chem. B40, 333 (1938).

[85] O.V. Krylov and S.Z. Roginsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2 (1956).

[86] G. Joris, I. Jungers and H. Taylor, J. Am. Chem. Soc. 60, 1982 (1938).

[87] V.N. Ipatieff, B.B. Corson and J.D. Kurbatov, J. Phys. Chem. 43, 589 (1939); B.B. Corson and V.N. Ipatieff, J. Phys. Chem. 45, 431 (1941).

[88] T. Tucholski and E. Rideal, J. Chem. Soc. 1701 (1935).

[89] R. Klar, Z. phys. Chem. A174, 1 (1935).

[90] G. Melkonian and B. Reps, Z. Elektrochem. 58, 616 (1964).

[91] R. Beebe, G.W. Low, F. Wildner and S. Goldwasser, J. Am. Chem. Soc. 57, 2577 (1935). I. Soller, S. Goldwasser and R. Beebe, J. Am. Chem. Soc. 58, 1703 (1936).

[92] E.B. Maxted and C. Moon, J. Chem. Soc. 1542 (1936).

[93] H.W. Melville and E.K. Rideal, Proc. Roy. Soc. A153, 77, 89 (1935)

[94] S. Iijima, Rep. Phys. Chem. Japan 12, 83 (1938).

[95] A. Magnus and G. Sartori, Z. phys. Chem. A175, 329 (1936); R. Klar, Naturwiss. 22, 822 (1934). R. Klar, Z. Electrochem. 43, 379 (1937).

[96] J. Pace and H. Taylor, J. Chem. Phys. 2, 578 (1934).

[97] H.W. Kohlschritter, Z. phys. Chem. A170, 300 (1934).

[98] H. Taylor and W. Bleakney, Phys. Rev. 43, 496 (1933); A. Gould, W. Bleakney and H. Taylor, J. Chem. Phys. 2, 362 (1934); H. Taylor and E. Schmidt, J. Am. Chem. Soc. 60, 367 (1938).

[99] J.H. Hudson and G. Ogden, Nature 142, 476 (1938).

[100] K. Peters and W. Lomas, Z. phys. Chem. A180, 51 (1937); Angew. Chem. 50, 46 (1937).

[101] P. Harteck and R. Edse, Angew. Chem. 53, 210 (1940).

[102] G. Beggerow and P. Harteck, Z. phys. Chem. A193, 265 (1944).

[103] P. Harteck and G. Melkonian, Naturwiss. 19, 450 (1950).

[104] E.A. Gulbarsen and A. Kennett, J. Electrochem. Soc. 101, 560 (1954).

[105] W. Jost and A. Widman, Z. phys. Chem. B29, 247 (1935).

[105a] R. Jouan, J. phys. Radium 7, 101 (1936).

[106] G.M. Zhabrova, S.Z. Roginsky and E.A. Fokina, Proc. Acad. Sci. USSR 52, 315 (1946). G.M. Zhabrova and E.A. Fokina, Problems of Kinetics and Catalysis 6, 151 (1949)

[107] M. Orchin, Adv. Catal. 5, 385 (1953).

[108] R. Bernstein, J. Phys. Chem. 56, 893 (1952); J. Chem. Phys. 22, 710 (1954).

[109] A. Garaff and H. Tompson, J. Chem. Soc. 1822 (1934).

[110] C. Bawn, Trans. Far. Soc. 31, 440 (1935).

[111] K. Tonosaki and B. Sugiuma, Bull. Inst. Phys. Chem. Res. (Tokyo) 22, 1014 (1943)

[112] B. Crowford and P. Cross, J. Chem. Phys. 6, 525 (1938).

[113] A.I. Shatenshtein, Theory of Acids and Bases; Moscow - Leningrad, State Chem. Press (1949).

[114] J. Butler, F. Rothstein, R. Bell and M. Kilpatrick, Katalyse in Lösungen. Handb. der Katalyse B. 2, (1940)

[115] R.P. Bell, Adv. Catal. 4, 151 (1952).

[116] M.I. Usanovich, J. Gen. Chem. 9, 182 (1939).

[117] M.I. Shatenshtein, Progr. Chem. 16, 548 (1947).

[118] T. Lowry and I. Faulkner, J. Chem. Soc. 2883 (1925); T. Lowry, ibid. 2554 (1927).

[119] C. Ingold and C. Wilson, J. Chem. Soc. 93 (1934); S. Hsü, C. Ingold and C. Wilson, ibid. 1778 (1935).

[120] S. Swain, J. Am. Chem. Soc. 72, 4578 (1950).

[121] G.P. Miklukhin, Progr. Chem. 17, 667 (1948).

[122] G. Schwarzenbach, Z. Elektrochem. 44, 46 (1938).

[123] O. Reitz, Z. Elektrochem. 44, 72 (1938).

[124] O. Reitz, Katalyse in Lösungen. Handb. der Katalyse 2, 272 (1940).

[125] E.A. Moelwyn-Hughes, Z. phys. Chem. B26, 272 (1934); E.A. Moelwyn-Hughes and K.F. Bonhoeffer, Naturwiss. 22, 174 (1934).

[126] P. Gross, H. Suess and H. Steiner, Naturwiss. 22, 662 (1934); P. Gross, H. Steiner and H. Suess, Trans. Far. Soc. 32, 883 (1936).

[127] E.A. Moelwyn-Hughes, R. Klar and K.F. Bonhoeffer, Z. phys. Chem. A169, 113 (1934).

[128] W.H. Hamill and V.K. La Mer, J. Chem. Phys. 4, 395 (1936).

[129] J.C. Hornel and J.A.V. Butler, J. Chem. Soc. 1361 (1936).

[130] F. Brescia and V.K. La Mer, J. Am. Chem. Soc. 60, 1962 (1938).

[131] W.J.C. Orr and J.A.V. Butler, J. Chem. Soc. 330 (1937).

[132] W.E. Nelson and J.A.V. Butler, J. Chem. Soc. 957 (1938).

[133] K. Schwarz, Z. Elektrochem. 40, 474 (1934); Akad. Anzeiger Wien 26,(April, 1934).

[134] O. Reitz, Z. phys. Chem. A183, 371 (1939).

[135] O. Reitz, Z. Elektrochem. 43, 659 (1937).

[136] O. Reitz and J. Kopp, Z. phys. Chem. A184, 429 (1939).

[137] P. Gross, H. Steiner and F. Krauss, Trans. Far. Soc. 32, 877 (1936); 34, 351 (1938).

[138] S.H. Maron and V.K. La Mer, J. Am. Chem. Soc. 61, 692 (1939).

[139] H. Stamm and M. Goehring, Z. phys. Chem. A183, 112 (1938).

[140] K. Wiberg, Chem. Rev. 55, 713 (1955).

[141] W.F.K. Wynne-Jones, Chem. Rev. 17, 115 (1935).

[142] O. Reitz, Z. phys. Chem. A177, 85 (1936).

[143] E. Abel and F. Fabian, Oesterr. Chem.-Ztg. 40, 26 (1937).

[144] E. Abel and F. Fabian, Monatsh. 71, 153 (1938).

[145] B. Pacsu, J. Am. Chem. Soc. 56, 745 (1934).

[146] W.F.K. Wynne-Jones, J. Chem. Phys. 2, 381 (1934).

[147] W.H. Hamill and V.K. La Mer, J. Chem. Phys. 2, 891 (1934); 4, 144 (1936).

[148] V.K. La Mer and J. Greenspan, Trans. Far. Soc. 33, 1266 (1937); V.K. La Mer, Chem. Rev. 19, 363 (1936).

[149] S. Liotta and V.K. La Mer, J. Am. Chem. Soc. 60, 1867 (1938).

[150] S.H. Maron and V.K. La Mer, J. Am. Chem. Soc. 60, 2588 (1938).

[151] O. Reitz, Z. phys. Chem. A176, 363 (1936).

[152] C.L. Wilson, J. Chem. Soc. 1550 (1936).

[153] E.J. Ives and G.C. Wilks, J. Chem. Soc. 1455 (1938).

[154] A. Lapworth, J. Chem. Soc. 30 (1904).

[155] H. Dawson and F. Pours, J. Chem. Soc. 2135 (1913).

[156] K.J. Pedersen, J. Phys. Chem. 37, 751 (1933); 38, 601 (1934).

[157] R.P. Bell and O.M. Lidwell, Proc. Roy. Soc. A176, 88 (1940).

[158] R.P. Bell and A.D.S. Tantram, J. Chem. Soc. 370 (1948).

[159] G. Schwarzenbach and C. Wittwer, Helv. Chim. Acta 30, 669 (1947).

[160] C.K. Ingold and C.L. Wilson, J. Chem. Soc. 773 (1934).

[161] O. Reitz, Z. phys. Chem. A179, 119 (1937).

[162] C.L. Wilson, J. Chem. Soc. 1550 (1936).

[163] W.D. Walters and K.F. Bonhoeffer, Z. phys. Chem. A182, 265 (1938).

[164] D. Turnbull and S. Maron, J. Am. Chem. Soc. 65, 212 (1943).

[165] N. Kornblum, N. Lichtin, J. Patton and D. Iffland, J. Am. Chem. Soc. 69, 307 (1947); N. Kornblum, J. Patton and J. Nordmann, ibid. 70, 764 (1948).

[166] J. Houben, Methods of Organic Chemistry, Moscow, State Chem. Press (1949).

[167] E.D. Hughes, C.K. Ingold and R.I. Reed, Nature 158, 448 (1946); R.P. Gillespie, J. Graham, E.D. Hughes, C.K. Ingold and E.R.P. Peeling, Nature 158, 480 (1946).

[168] R.E. Gillespie and D.J. Millen, Quart. Rev. Chem. Soc. 2, 277 (1948).

[169] L. Melander, Nature 163, 599 (1949).

[170] L. Melander, Acta. Chem. Scand. 3, 95 (1949); Arkiv. Kemi 2, 213 (1950); T.G. Bonner, F. Bowyer and G. Williams, J. Chem. Soc. 2650 (1953).

[171] G. Bennet, J. Brand, J. Tames, D. Saunders and T. Williams, J. Chem. Soc. 474 (1947).

[172] C.K. Ingold, Structure and Mechanism in Organic Chemistry (New York, 1953).

[173] K.H. Geib, Elektrochem. 44, 81 (1938).

[174] I. Amdur, J. Am. Chem. Soc. 57, 856 (1935).

[175] A. Farkas and L. Farkas, Proc. Roy. Soc. A152, 124 (1935).

[176] K. Geib and B. Steacie, Z. phys. Chem. B29, 215 (1935).

[177] A. Farkas and H.W. Melville, Proc. Roy. Soc. A157, 625 (1936); H.W. Melville, Proc. Roy. Soc. A157, 621 (1936).

[178] J.L. Bolland and H. Melville, Proc. Roy. Soc. A160, 384 (1937).

[179] C.E.H. Bawn and A.G. Evans, Trans. Far. Soc. 31, 1392 (1935).

[180] A. Farkas and L. Farkas, Naturwiss. 22, 218 (1934).

[181] G.K. Rollefson, J. Am. Chem. Soc. 56, 579 (1934).

[182] F. Bach, K. Bonhoeffer and E.A. Moelwyn-Hughes, Z. phys. Chem. B27, 71 (1934).

[183] K. Geib and A. Lendle, Z. phys. Chem. B32, 463 (1936).

[184] J.G.L. Blagg and G.M. Murphy, J. Chem. Phys. 4, 631 (1936).

[185] A. Wheeler and R.N. Pease, J. Am. Chem. Soc. 58, 1665 (1936).

[186] G.K. Rollefson, J. Chem. Phys. 2, 144 (1934).

[187] W.M. Jones, J. Chem. Phys. 19, 78 (1951).

[188] M. Van Meersche, Bull. Soc. Chim. Belges 60, 99 (1951).

[189] G. Boato, G. Careri, A. Cimino, E. Molinari and G. Volpi, XIII Intern. Congr. of Pure and Appl. Chem. (Stockholm, 1953).

[190] T.G. Majury and E.W. Steacie, Disc. Far. Soc. No. 14, 45 (1953).

[191] E.W. Steacie, Atomic and Free Radical Reactions (New York, 1946).

[192] E.W. Steacie, Atomic and Free Radical Reactions, 2nd ed. (New York, 1954).

[193] M.H.J. Wijnen and E.W. Steacie, J. Chem. Phys. 20, 205 (1952).

[194] R.D. Anderson, S. Davison and M. Burton, Disc. Far. Soc. 10, 136 (1951).

[195] B. de B. Darwent and R. Roberts, Disc. Far. Soc. 14, 55 (1953).

[196] N.N. Semenov, Chain Reactions, Moscow, United Sci.-Tech. Press (1934).

[197] K. Bonhoeffer and P. Harteck, Principles of Photochemistry, Moscow, United Sci.-Tech. Press (1935).

[198] S.D. Cooley and R.B. Anderson, J. Am. Chem. Soc. 77, 235 (1955).

[199] Ya.B. Zeldovich and D.A. Frank-Kamenetsky, J. Phys. Chem. 12, 100 (1938); Ya.B. Zeldovich, Theory of the Combustion and Detonation of Gases, Moscow, Acad. Sci. USSR Press (1944).

[200] C. Tanford and R.N. Pease, J. Chem. Phys. 15, 861 (1947).

[201] D.R. Stranks, Trans. Far. Soc. 51, 514 (1955).

[202] B. Lewis and G. von Elbe, Combustion, Flames, and Explosions of Gases, Moscow, Foreign Lit. Press (1948).

[203] C.N. Hinshelwood and A.T. Williamson, The reaction between hydrogen and oxygen (Oxford, 1934).

[204] W.A. Noyes and P.A. Leighton, The Photochemistry of Gases (New York, 1941).

[205] S.C. Lind, The chemical effects of alpha particles and electrons (New York, 1928); A.B. Shekhter, Problems of Kinetics and Catalysis. 2. Chemical Reactions in Electric Discharges (1935).

[206] A.L. Marshall, J. Am. Chem. Soc. 50, 3197 (1928).

[207] G. Glockler and S.C. Lind, The Electrochemistry of Gases (1939).

[208] L.M. Dorfman and B.A. Flemmer, J. Chem. Phys. 22, 1555 (1954).

[209] I.P. Selinov, Atomic Nuclei and Nuclear Transformations, Moscow, State Tech. Press (1951).

[210] H.W. Melville, J. Chem. Soc. 797, 1234 (1934).

[211] A.A. Frost and Alyea, J. Am. Chem. Soc. 56, 1251 (1934); C.N. Hinshelwood et al., Nature 133, 947 (1934).

[212] N.F.H. Bright and R.P. Hagerty, Trans. Far. Soc. 43, 697 (1947).

[213] A.H. Taylor and R.H. Crist, J. Am. Chem. Soc. 63, 1377 (1941).

[214] M. Bodenstein, Z. phys. Chem. 13, 56 (1894); 22, 1 (1897); 29, 295 (1899).

[215] S.W. Benson and R. Srinivasan, J. Chem. Phys. 23, 200 (1955).

[216] G. Lewis and E.K. Rideal, J. Am. Chem. Soc. 48, 2553 (1926).

[217] H.L. Friedman, R.B. Bernstein and H.E. Gunning, J. Chem. Phys. 23, 109 (1955).

[218] H.G. Grimm and E. Schwamberger, Rev. Ind. Chim. Phys. (Paris, 1926), p. 214.

[219] F.T. Lessig, J. Phys. Chem. 36, 2325 (1932).

[220] P. Fugassi and F. Daniels, J. Am. Chem. Soc. 60, 771 (1938).

[221] B. Daniels and P.L. Veltman, J. Chem. Phys. 7, 756 (1939).

[222] J.B. Peri and F. Daniels, J. Am. Chem. Soc. 72, 424 (1950).

[223] A.T. Blades and G.M. Murphy, J. Am. Chem. Soc. 74, 6219 (1952); C.H. Leigh and M. Szwarc, J. Chem. Phys. 20, 403 (1952).

[224] J. Bigeleisen and M. Wolfsberg, J. Chem. Phys. 21, 1972 (1953).

[225] J. Bigeleisen and M. Wolfsberg, J. Chem. Phys. 22, 1264 (1954).

[226] M. Cohen and E.H. Wesheimer, J. Am. Chem. Soc. 74, 4387 (1952).

[227] V.J. Shiner, J. Am. Chem. Soc. 74, 5285 (1952).

[228] L. Melander, Arkiv Kemi 2, 211 (1950).

[229] E.S. Lewis and C.E. Boozer, J. Am. Chem. Soc. 74, 6306 (1952); 76, 791, 794 (1954).

[230] H. Gilman, G.E. Dunn and G.S. Hammond, J. Am. Chem. Soc. 73, 4499 (1951).

[231] L. Kaplan and K.E. Wilzbach, J. Am. Chem. Soc. 74, 6152 (1952).

[232] L. Kaplan and K.E. Wilzbach, J. Am. Chem. Soc. 77, 1297 (1955).

CHAPTER V

KINETICS OF COMPLICATED ISOTOPIC EXCHANGE

§ 1. Main Types of Complications

Until recently the kinetics of isotopic exchange had been worked out in detail only for the simplest case of exchange of atoms or groups between two substances, each of which contains one atom of the particular element in its molecule. Attempts were made to reduce all the more complex cases to this case, represented by the equation

$$AX + B\overset{*}{X} \rightleftarrows A\overset{*}{X} + BX. \qquad (1)$$

Both homogeneous and catalytic heterogeneous reactions of this type conform to exponential kinetic equations, whatever the actual exchange mechanism, and with any deviations of the system from ideality [1, 2].

The extension of the range of applications of isotope methods in chemistry made it necessary to develop a theory applicable to more complex systems. Some definite successes have been achieved in this respect in recent years, but the problem is not yet completely solved, partly because of the serious difficulties which have arisen in mathematical analysis of the problem, and partly because the exchange mechanisms are not sufficiently well understood. In investigations of exchange in chemical reactions the isotopic exchange generally occurs in complicated conditions and we have therefore attempted to fill the existing gap by an examination of the kinetics and general laws of complicated exchange, with a more detailed analysis of some limiting cases, which seemed to be the most typical of systems met in studies of chemical mechanisms [3, 4].

Complications of the kinetics of isotopic exchange may originate from several causes. These may be:

a) the existence of more than two forms involved in the exchange, under phase conditions which lead to uncomplicated exchange if two forms are present;

b) the existence of two or more phases in the system;

c) phase inhomogeneity;

d) slow material transfer under various diffusion and diffusion-kinetic conditions;

e) a peculiar set of complications, arising in the simultaneous occurrence of ordinary "elementary" chemical reactions and isotopic exchange reactions of the same substances which do not involve changes of elementary composition or chemical structure of the molecules.

§ 2. Complications of Isotopic Exchange Kinetics Caused by the Participation of More than Two Forms

This very common type of complicated exchange naturally falls into two more special groups.

The first group includes isotopic exchange reactions, in which more than two kinds of substances are involved, for example:

$$\begin{aligned} &A_1X + A_2X + \ldots + B_1\overset{*}{X} + B_2\overset{*}{X} + \ldots \rightleftarrows \\ &\rightleftarrows A_1\overset{*}{X} + A_2\overset{*}{X} + \ldots + B_1X + B_2X \ldots \end{aligned} \qquad (2)$$

Of great interest kinetically is a particular type of reaction in this group in which the complication is caused by the presence or formation in the system, in addition to ordinary slowly exchanging molecules, of rapidly exchanging active molecules of the same substances. These may be radicals, ions, tautomeric active forms, metastable electronically excited molecules, etc. The active forms Y may exist in mobile thermodynamic equilibrium with ordinary molecules, or they may arise under the action of external radiation or in side chemical reactions at considerably greater than equilibrium concentrations. If the presence of these forms is to lead to specific effects in the kinetics of isotopic exchange, and not to reduce to trivial participation of Arrhenius-type active particles in the exchange, the average life of an unusual active molecule τ_y should be long enough for more than one unit isotopic exchange reaction before the Y molecule is deactivated by conversion into the usual form. This conditions is contrary to the behavior of active molecules according to Lindemann's molecular-kinetic theory of monomolecular reactions [5, 6]. The exchange, in presence of active forms with sufficiently large τ_y, is represented by the equations

$$\left.\begin{array}{l} 1)\ AX + B\overset{*}{X} \xrightarrow{\text{slow}} A\overset{*}{X} + BX \\ 2)\ AX \rightarrow Y \\ 3)\ Y + B\overset{*}{X} \xrightarrow{\text{rapid}} \overset{*}{Y} + BX \\ 4)\ \overset{*}{Y} \rightarrow A\overset{*}{X} \end{array}\right\} \qquad (3)$$

In the Eqs. (3), Y represents AX in the unusual active state, while $\overset{*}{Y}$ represents $A\overset{*}{X}$ in the same state. For simplicity only the forward reactions are shown. For new kinetic effects to appear, direct isotopic exchange by Eq. (3,1) must be considerably slower than the same exchange effected by combination of the steps (3,2), (3,3), and (3,4). For simplicity, we do not consider instances when isotopic exchange by this scheme involves several types of "metastable" active molecules simultaneously.

The second group of isotopic exchange reactions with an increase in the number of participating forms includes exchange reactions in which a molecule of at least one of the exchanging substances contains more than one atom of the particular isotope, if not all the atoms are present in the molecule in identical structural positions.

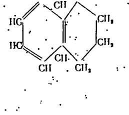
For example, this group of reactions includes the exchange of the anhydride of monochloroacetic acid with hydrogen chloride

$$CH_2ClCOCl + H\overset{*}{Cl} \begin{array}{l} \nearrow CH_2\overset{*}{Cl}\,COCl + HCl \\ \searrow CH_2Cl\,CO\overset{*}{Cl} + HCl \end{array}\Bigg\} \qquad (4)$$

On the other hand, the exchange of carbon dioxide with water vapor or of aluminum iodide with I_2 does not belong to this group

$$\left.\begin{array}{l} Al_2I_6 + I\overset{*}{I} \rightarrow Al_2I_5\overset{*}{I} + I_2; \\ CO_2^{16} + H_2O^{18} \rightarrow CO^{16}O^{18} + H_2O^{16}. \end{array}\right\} \qquad (5)$$

For simplicity, Eqs. (4) and (5) do not show the products of twofold and higher substitution. Isotopic hydrogen exchange is characterized by the presence in the exchanging molecules of several types of hydrogen atoms, with different reactivities, and each type may contain several atoms. Thus, in the tetralin molecule



according to N. M. Dykhno and A. I. Shatenshtein [7], three types of H atoms can be clearly distinguished according to the rates of exchange with deuteroammonia. Four hydrogen atoms of the hexamethylene ring (presumably the hydrogen atoms of the α methylene groups) exchange particularly easily at room temperature. In the same conditions four hydrogen atoms of the aromatic ring exchange 70-100 times less rapidly, and finally, four hydrogen atoms of the β-methylene groups of the hexamethylene ring exchange at least 100 times more slowly still; and the authors were not able to detect this exchange. The differences of the exchange rates of hydrocarbon hydrogens are more pronounced in acidic than in basic solvents. Thus, in the exchange of hydrogen between aromatic hydrocarbons and deuterium bromide which was studied in detail by V. R. Kalinachenko et al. [8], sharp differences were found between the rates of exchange of hydrogen atoms in the α- and β-positions in naphthalene. This is shown in Table 98.

TABLE 98

Rate Constants for the Isotopic Exchange of Hydrogen in the α- and β-Positions in Naphthalene with Deuterium Bromide. After Kalinachenko

T, °C	35	25	0	−40	−50
α atoms	—	$\sim 3\cdot10^{-3}$	$2\cdot10^{-3}$	$\sim 7\cdot10^{-4}$	$\sim 3\cdot10^{-4}$
β atoms	$\sim 9\cdot10^{-5}$	$\sim 7\cdot10^{-5}$	$6\cdot10^{-5}$	—	—

In liquid deuteroammonia the rates of exchange of α- and β-atoms in naphthalene practically coincide. According to A. I. Shatenshtein and E. A. Izrailevich [8], at a potassamide concentration of 0.01 N, $k = 10^7$ exp (14200/RT). It seems that the approximately 40-fold difference of exchange rates observed in deuteriumbromide is caused by different values of the pre-exponential terms, with the same activation energy of 0.3-0.4 kcal/mole.

In alkylated aromatic hydrocarbons the number of types of hydrogen with different exchange reactivities is still larger. For example, in some of the monoalkyl benzenes which have been studied (toluene, ethylbenzene, isopropylbenzene, n-butylbenzene, and isobutylbenzene) the hydrogen in the para-position is exchanged more rapidly than the others, with a rate constant $k = 10^{-4}\ \mathrm{sec}^{-1}$ at 25°C. For hydrogen in the ortho-position $k = 10^{-5}\ \mathrm{sec}^{-1}$, and in the meta-position $k = 3\cdot10^{-7}\ \mathrm{sec}^{-1}$. The value of k for the alkyl hydrogen is still lower. It has so far eluded determination. It is probable that the exchange rate constants of hydrogen atoms attached to different carbon atoms in the alkyl groups are also different, but because of the exchange inertness of alkyl hydrogen these differences have not yet been detected. It is evident that in compounds with other functions (acids, hydroxy acids, amines, heterocyclic compounds of various functions, etc.) the number of types of hydrogen atoms is greater than in hydrocarbons, and in hydrogen exchange of such compounds a still greater number of exchange rate constants must be taken into account.

The same paper contains instructive data on differences in the exchange rates of aromatic hydrogen in related compounds (Table 99).

TABLE 99

Comparison of Rate Constants for the Isotopic Exchange of Hydrogen in Aromatic Rings with DBr at Room Temperature [8]

Hydrocarbon	k
Benzene	$5\cdot10^{-8}\ \mathrm{sec}^{-1}$
Toluene	$9\cdot10^{-6}\ \mathrm{sec}^{-1}$
Diphenylmethane	$\sim 2\cdot10^{-6}\ \mathrm{sec}^{-1}$
Triphenylmethane	$\sim 5\cdot10^{-7}\ \mathrm{sec}^{-1}$

Methylbenzenes with different numbers of methyl hydrogen atoms, such as toluene, mesitylene, durene, and hexamethylbenzene, differ considerably in their rates of exchange with deuteroammonia.

If two or more related compounds are present simultaneously in a solution, each exchanges at its characteristic rate, independently of the others. It must be emphasized that, in exchange with concentrated deuterium donors, the simultaneous formation of all the possible deutero-substituted hydrocarbons – monodeuterated, dideuterated, etc, up to completely deuterated molecules, must be taken into consideration. In the general case, exchange may involve several kinds of molecules simultaneously, and some of these may each contain several atoms of the exchanging element in different chemical states. The principal kinetic laws for the two above groups of reactions are analogous, but the two groups differ essentially in the chemical sense.

In all cases when several molecular forms or several atoms within the molecules are involved in isotopic exchange, it is necessary to take into account the possibility of additional direct isotopic exchange between different acceptors, or between different atoms within the acceptor molecules, exchanging with the same deuterium or tritium donor.

§ 3. Transfer and Conjugation in Isotopic Exchange

In isotopic exchange represented by Eq. (2), in addition to exchange of molecules of each of the substances A_1X, A_2X, etc., with molecules of $B_1\overset{*}{X}$, $B_2\overset{*}{X}$

$$\left.\begin{aligned} A_1X + B_1\overset{*}{X} &\rightarrow A_1\overset{*}{X} + B_1X,\\ A_2X + B_1\overset{*}{X} &\rightarrow A_2\overset{*}{X} + B_1X,\ldots\\ A_1X + B_2\overset{*}{X} &\rightarrow A_1\overset{*}{X} + B_2X,\ \text{etc.}\end{aligned}\right\} \quad (2a)$$

it is necessary to take into account the possibility of isotopic exchange of $A_1\overset{*}{X}$ with A_2X, of $B_1\overset{*}{X}$ with B_2X, etc.

$$\left.\begin{aligned} A_1\overset{*}{X} + A_2X &\rightarrow A_2\overset{*}{X} + A_1X,\\ B_1\overset{*}{X} + B_2X &\rightarrow B_2\overset{*}{X} + B_1X,\ \text{etc.}\end{aligned}\right\} \quad (2b)$$

As soon as the system begins to contain appreciable amounts of tagged molecules of any of the substances $A_i\overset{*}{X}$, or the concentration of any of the substances $B_\alpha\overset{*}{X}$ decreases as the result of exchange with A_iX, the reactions of Eq. (2b) become possible in principle.

Such complications, associated with the possibility of intramolecular processes, occur in isotope exchange between molecules $AX'_mX''_nX'''_p$ and $BX'_rX''_s$ containing atoms of X in different chemical states or in different structural positions X', X", X‴, etc. Suppose that initially the isotope $\overset{*}{X}$ is present only in the substance BX'_rX'', for example, as molecules of $B\overset{*}{X}'_rX''_s$; then even without participation of AX_z ($z = m + n + p$), intramolecular exchange of $\overset{*}{X}$ in one position with X in another may occur, leading to the formation of molecules of $B\overset{*}{X}'_{r-1}X'X''_{s-1}\overset{*}{X}''$, $B\overset{*}{X}'_{r-2}X'_2X''_{s-2}\overset{*}{X}''_2$, etc. In exchange with AX_z molecules, the number of possible subsidiary exchange reactions greatly increases. For instance, if in molecules of AX_z, where $z = m + n + p$, X' atoms exchange much more rapidly than X" and X‴ atoms, exchange with $B\overset{*}{X}_y$ ($y = r + s$) will initially produce molecules of $A\overset{*}{X}'X'_{m-1}X''_nX'''_p$; $A\overset{*}{X}'_2X'_{m-2}X''_nX'''_p$; $A\overset{*}{X}'_3X'_{m-3}X''_nX'''_p$, etc. These molecules can take part in subsidiary exchange processes involving X atoms in three positions. Because of this, if the direct exchange of X" and X‴ atoms with the $\overset{*}{X}$ isotope in the BX_y molecules is negligibly slow, this isotope may appear in all three structural positions in the AX_z molecule. Consequently, several subsidiary reactions of isotope redistribution within the molecules will be superposed upon the initial process of direct exchange of X isotopes between AX_z and BX_y. In practice, all intermediate cases between negligibly slow and immeasurably rapid exchange of the subsidiary forms are met, which makes determinations of the exchange rates of different types of molecules in mixtures, or individual atoms in a complex molecule containing a particular element in several chemical forms, impossible.

An example of the practically independent exchange of the components of a mixture is provided by the isotopic exchange of aluminum bromide with a mixture of two organic bromides. This process was studied by us jointly with N. E. Brezhneva and A. I. Shilinsky [9] for binary mixtures of ethyl bromide with ethylene bromide $C_2H_4Br_2$, isoamyl bromide, and bromoform. Taken in pairs or in more complex groups, these bromides practically according to N. M. Dykhno and A. I. Shatenshtein [7], three types of H atoms can be clearly distinguished according to the rates of exchange with deuteroammonia. Four hydrogen atoms of the hexamethylene ring (presumably the hydrogen atoms of the α-methylene groups) exchange particularly easily at room temperature. In the same conditions four hydrogen atoms of the aromatic ring exchange 70-100 times less rapidly, and finally, four hydrogen atoms of the β-methylene groups of the hexamethylene ring exchange at least 100 times more slowly still, and the authors were not able to detect this exchange. The differences of the exchange rates of hydrocarbon hydrogens are more pronounced in acidic than in basic solvents. Thus, in the exchange of hydrogen between aromatic hydrocarbons and deuterium bromide which was studied in detail by V. R. Kalinachenko et al. [8], sharp differences were found between the rates of exchange of hydrogen atoms in the α- and β-positions in naphthalene. This is shown in Table 98.

TABLE 98

Rate Constants for the Isotopic Exchange of Hydrogen in the α- and β-Positions in Naphthalene with Deuterium Bromide, After Kalinachenko

T, °C	35	25	0°	−40	−50
α atoms	—	$\sim 3 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$\sim 7 \cdot 10^{-4}$	$\sim 3 \cdot 10^{-4}$
β atoms	$\sim 9 \cdot 10^{-5}$	$\sim 7 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	—	—

In liquid deuteroammonia the rates of exchange of α- and β-atoms in naphthalene practically coincide. According to A. I. Shatenshtein and E. A. Izrailevich [8], at a potassamide concentration of 0.01 N, $k = 10^7 \exp(-14200/RT)$. It seems that the approximately 40-fold difference of exchange rates observed in deuterium bromide is caused by different values of the pre-exponential terms, with the same activation energy of 0.3-0.4 kcal/mole.

In alkylated aromatic hydrocarbons the number of types of hydrogen with different exchange reactivities is still larger. For example, in some of the monoalkyl benzenes which have been studied (toluene, ethylbenzene, isopropylbenzene, n-butylbenzene, and isobutylbenzene) the hydrogen in the para-position is exchanged more rapidly than the others, with a rate constant $k = 10^{-4}\ \mathrm{sec}^{-1}$ at 25°C. For hydrogen in the ortho-position $k = 10^{-5}\ \mathrm{sec}^{-1}$, and in the meta-position $k = 3 \cdot 10^{-7}\ \mathrm{sec}^{-1}$. The value of k for the alkyl hydrogen is still lower. It has so far eluded determination. It is probable that the exchange rate constants of hydrogen atoms attached to different carbon atoms in the alkyl groups are also different, but because of the exchange inertness of alkyl hydrogen these differences have not yet been detected. It is evident that in compounds with other functions (acids, hydroxy acids, amines, heterocyclic compounds of various functions, etc.) the number of types of hydrogen atoms is greater than in hydrocarbons, and in hydrogen exchange of such compounds a still greater number of exchange rate constants must be taken into account.

The same paper contains instructive data on differences in the exchange rates of aromatic hydrogen in related compounds (Table 99).

TABLE 99

Comparison of Rate Constants for the Isotopic Exchange of Hydrogen in Aromatic Rings with DBr at Room Temperature [8]

Hydrocarbon	k
Benzene	$5 \cdot 10^{-8}\ \mathrm{sec}^{-1}$
Toluene	$9 \cdot 10^{-6}\ \mathrm{sec}^{-1}$
Diphenylmethane	$\sim 2 \cdot 10^{-6}\ \mathrm{sec}^{-1}$
Triphenylmethane	$\sim 5 \cdot 10^{-7}\ \mathrm{sec}^{-1}$

Methylbenzenes with different numbers of methyl hydrogen atoms, such as toluene, mesitylene, durene, and hexamethylbenzene, differ considerably in their rates of exchange with deuteroammonia.

If two or more related compounds are present simultaneously in a solution, each exchanges at its characteristic rate, independently of the others. It must be emphasized that, in exchange with concentrated deuterium donors, the simultaneous formation of all the possible deutero-substituted hydrocarbons – monodeuterated, dideuterated, etc., up to completely deuterated molecules, must be taken into consideration. In the general case, exchange may involve several kinds of molecules simultaneously, and some of these may each contain several atoms of the exchanging element in different chemical states. The principal kinetic laws for the two above groups of reactions are analogous, but the two groups differ essentially in the chemical sense.

In all cases when several molecular forms or several atoms within the molecules are involved in isotopic exchange, it is necessary to take into account the possibility of additional direct isotopic exchange between different acceptors, or between different atoms within the acceptor molecules, exchanging with the same deuterium or tritium donor.

§3. Transfer and Conjugation in Isotopic Exchange

In isotopic exchange represented by Eq. (2), in addition to exchange of molecules of each of the substances A_1X, A_2X, etc., with molecules of $B_1\overset{*}{X}$, $B_2\overset{*}{X}$

$$\left.\begin{aligned} A_1X + B_1\overset{*}{X} &\to A_1\overset{*}{X} + B_1X, \\ A_2X + B_1\overset{*}{X} &\to A_2\overset{*}{X} + B_1X, \\ A_1X + B_2\overset{*}{X} &\to A_1\overset{*}{X} + B_2X, \text{ etc.} \end{aligned}\right\} \qquad (2a)$$

it is necessary to take into account the possibility of isotopic exchange of $A_1\overset{*}{X}$ with A_2X, of $B_1\overset{*}{X}$ with B_2X, etc.,

$$\left.\begin{aligned} A_1\overset{*}{X} + A_2X &\to A_2\overset{*}{X} + A_1X, \\ B_1\overset{*}{X} + B_2X &\to B_2\overset{*}{X} + B_1X, \text{ etc.} \end{aligned}\right| \qquad (2b)$$

As soon as the system begins to contain appreciable amounts of tagged molecules of any of the substances $A_i\overset{*}{X}$, or the concentration of any of the substances $B_\alpha\overset{*}{X}$ decreases as the result of exchange with A_iX, the reactions of Eq. (2b) become possible in principle.

Such complications, associated with the possibility of intramolecular processes, occur in isotope exchange between molecules $AX'_mX''_nX'''_p$ and $BX'_rX''_s$ containing atoms of X in different chemical states or in different structural positions X', X'', X''', etc. Suppose that initially the isotope $\overset{*}{X}$ is present only in the substance $BX'_rX''_s$, for example, as molecules of $B\overset{*}{X}{}'_rX''_s$; then even without participation of AX_z $(z = m + n + p)$, intramolecular exchange of $\overset{*}{X}$ in one position with X in another may occur, leading to the formation of molecules of $B\overset{*}{X}{}'_{r-1}X'X''_{s-1}\overset{*}{X}{}''$, $B\overset{*}{X}{}'_{r-2}X'_2X''_{s-2}\overset{*}{X}{}''_2$, etc. In exchange with AX_z molecules, the number of possible subsidiary exchange reactions greatly increases. For instance, if in molecules of AX_z, where $z = m + n + p$, X' atoms exchange much more rapidly than X'' and X''' atoms, exchange with $B\overset{*}{X}_y$ $(y = r + s)$ will initially produce molecules of $A\overset{*}{X}{}'X'_{m-1}X''_nX'''_p$, $A\overset{*}{X}{}'_2X'_{m-2}X''_nX'''_p$; $A\overset{*}{X}{}'_3X'_{m-3}X''_nX'''_p$, etc. These molecules can take part in subsidiary exchange processes involving X atoms in three positions. Because of this, if the direct exchange of X'' and X''' atoms with the $\overset{*}{X}$ isotope in the BX_y molecules is negligibly slow, this isotope may appear in all three structural positions in the AX_z molecule. Consequently, several subsidiary reactions of isotope redistribution within the molecules will be superposed upon the initial process of direct exchange of X isotopes between AX_z and BX_y. In practice, all intermediate cases between negligibly slow and immeasurably rapid exchange of the subsidiary forms are met, which makes determinations of the exchange rates of different types of molecules in mixtures, or individual atoms in a complex molecule containing a particular element in several chemical forms, impossible.

An example of the practically independent exchange of the components of a mixture is provided by the isotopic exchange of aluminum bromide with a mixture of two organic bromides. This process was studied by us jointly with N. E. Brezhneva and A. L. Shilinsky [9] for binary mixtures of ethyl bromide with ethylene bromide $C_2H_4Br_2$, isoamyl bromide; and bromoform. Taken in pairs or in more complex groups, these bromides practically do not exchange with each other at moderate temperatures and in absence of catalysts. They exchange all their bromine with aluminum bromide, although at different rates (with complicating elementary reactions in the case of iso-$C_5H_{11}Br$). The rate of exchange with $AlBr_3$, measured on addition of tagged aluminum bromide to a mixture of two or several organic bromides, is the simple sum of the independent exchange rates for each of the organic bromides with the radioactive bromine donor $AlBr_3$.

However, despite the absence of direct exchange of bromine between R_1Br and R_2Br in presence of aluminum bromide, which may serve as a common donor of radioactive bromine for all the above organic bromides, transfer of bromine between the organic molecules inevitably occurs, and the isotopic composition ceases to be independent. The common donor begins to act as a catalytic carrier. This is a certain consequence of the reversibility of all isotopic exchange reactions, which leads to equipartition of isotopes between two rapidly exchanging compounds before the exchange has progressed far between two slowly exchanging compounds. If small amounts of inactive aluminum bromide are added to a mixture of two organic bromides, one of which contains radioactive bromine, rapid exchange of Br between the two organic halides occurs. The result of this exchange is equipartition of Br between the alkyl halides. The catalytic carrier of radioactive bromine, aluminum bromide, is, of course, involved in this equipartition. In this experiment the radioactive bromine donor is no longer $AlBr_3$, but one of the organic bromides, such as ethylene bromide, and the two acceptors are the other organic bromide and aluminum bromide. Because of the reversibility and the rapidity of the subsidiary exchange between the two acceptors R_2Br and $AlBr_3$, a single conjugated isotopic exchange process occurs in the system, instead of three independent exchange processes between the three pairs of substance. Conjugation is very common in isotopic exchange.

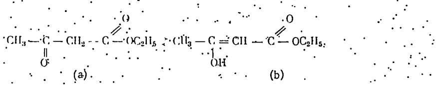
The above example shows that it is possible, by variations of the initial conditions, to bring about both limiting cases of complicated exchange – completely independent exchange without subsidiary exchange, and complete conjugation as the result of rapid subsidiary exchange – in the same system. An interesting fact is that in this instance, despite the sharp change in the nature of the exchange the inner mechanism of the exchange does not alter in the transition from simple binary exchange to complicated exchange in ternary and more complex mixtures.

§ 4 Conjugation Involving Tautomeric Regrouping

An important and widespread type of conjugated exchange is isotopic exchange in molecules capable of undergoing tautomeric transformations.

Tautomerism was discovered in 1873 by A. M. Butlerov [10, 11], and it has been proved for many organic compounds. Still more often its existence is postulated, without adequate proof, to explain the anomalous course of chemical reactions. In particular, until recently tautomerism has been assumed for all cases in which a substance forms two series of derivatives, corresponding to two isomeric forms. A. N. Nesmeyanov discovered such "dual reactivity" in absence of tautomerism [12-14] and determined its origin [15]. The concept of "pseudomerism," or tautomeric equilibrium displaced to the limit, has been severely criticized [16], and it has been shown that the formation of two series of derivatives is not a certain criterion of tautomerism. Tautomerism is real only in cases in which the tautomeric forms have been isolated or their contents have been proved and determined by direct methods, such as by absorption spectra, Raman spectra, or heat capacities.

The tautomerism of acetoacetic ester, which is of the keto-enol type, has been studied in great detail. The molecules of acetoacetic ester can exist in two forms: the ketonic (a) and the enolic (b), both of which have been isolated in pure form. If acetoacetic ester is cooled to a low temperature, the pure keto-form, which melts at −39°C, separates out. In special conditions it is possible to distill the enol-form in an almost pure state from acetoacetic ester, etc. In the ordinary state, a dynamic equilibrium exists between the two tautomeric forms; this can be represented by the equation

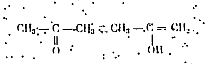


$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \rightleftharpoons CH_3-\underset{\underset{OH}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-OC_2H_5, \qquad (6)$$

(a) (b)

At equilibrium at room temperature, acetoacetic ester contains about 7% of the enol form.

Keto-enol tautomerism has been proved for ketones, in particular for acetone



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{OH}{|}}{C}=CH_2. \qquad (7)$$

There are numerous examples of keto-enol aromatic and hydroaromatic systems [17, 18]. Table 100 shows the equilibrium enol contents at room temperature for a number of compounds, in increasing order of enolization. The table begins with methyl acetoacetate with 4.8% enol, and ends with benzoylacetone with 98% enol. There is no doubt that the range of these variations is even wider; but very low and very high equilibrium concentrations of enols are difficult to determine exactly.

TABLE 100

Enol Contents in Liquid Keto-Enols, After Ingold [18]

Compound	Enol, %
Methyl acetoacetate	4.8
Ethyl acetoacetate	7.5
Methyl benzoylacetate	16.7
Ethyl benzoylacetate	29.2
Acetylacetone	80.4
Benzoylacetone	98.0

In the most typical cases tautomerism involves hydrogen atom displacement and migration of multiple bonds. Keto-enol tautomerism is only one type of triad system in which two carbon atoms and one oxygen atom are involved in the rearrangement of the molecule in tautomeric isomerization.

There are three-carbon triad systems, triad systems containing nitrogen, and systems with other numbers of atoms involved in the isomerization (diad, pentad, etc.). Tautomerism is not confined to organic compounds, and is met in inorganic chemistry. Table 101 illustrates some types of tautomeric triad systems.

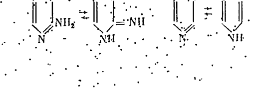
TABLE 101

Examples of Tautomeric Triad Systems.

Isomerization scheme	Name of system
$C(H)-C=C \rightleftharpoons C=C-C(H)$	Three-carbon
$C(H)-C=O \rightleftharpoons C=C-O(H)$	Keto-enol
$C(H)-C=N \rightleftharpoons C=C-N(H)$	Imino-N-amine
$C(H)-N=C \rightleftharpoons C=N-C(H)$	Methylene-azomethine
$C(H)-N=N \rightleftharpoons C=N-N(H)$	Azo-hydrazo
$N(H)-N=N \rightleftharpoons N=N-N(H)$	Diazo-amino

These are only a few of the number of possible types of tautomerism, to each of which correspond its own reversible addition reactions, similar in mechanism. For example, intramolecular keto-enol isomerization $C(H)-C=O \rightleftharpoons C=C-O(H)$ corresponds to aldol condensation [19] $C(H) + C=O \rightleftharpoons C-C-O(H)$. In this interpretation, the range of phenomena directly or indirectly related to tautomerism covers a large part of organic chemistry.

An example of a more complex type of tautomerism, involving rearrangement of the benzene ring, is the tautomerism of α- and γ-aminopyridines, discovered by A. E. Chichibabin [20]

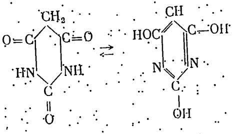


In substances which do not undergo tautomeric conversion, a sharp difference in the rates of hydrogen isotope exchange of hydroxyl hydrogen (OH) and of hydrogen linked to carbon (CH) with water has long been established. The first usually exchanges very rapidly (practically instantaneously), and the second, very slowly in absence of catalysts. Recently this has also been demonstrated for the exchange between methanol and ethanol in the gas phase [21].

On these grounds, in the keto forms of acetoacetic ester and acetone only very slow exchange of all the hydrogen atoms is to be expected, while the enol tautomers should exchange one hydrogen atom very rapidly and all the others extremely slowly. Experimental investigations [22] have shown that all the 6 hydrogen atoms in acetone can exchange with deuterium in water, and that this exchange is greatly accelerated by alkalies and moderately by acids. Five hydrogen atoms of acetoacetic ester are exchanged rapidly – three from the methyl and two from the methylene group – while hydrogen of the ethyl radical is not exchanged. Participation in exchange is a direct consequence of the dynamic tautomeric equilibrium. The simplest explanation would be to postulate alternate reversible transfer of all the hydrogen atoms linked to carbon atoms in the α-position to the carbonyl group, to the hydroxyl group, and exchange with deuterium in this position. A. I. Brodsky [23] has advanced serious arguments against this scheme, supporting an ionic mechanism involving the solvent. Considerable differences of exchange capacity are also found between hydrogens in C—H and N—H bonds, hydrogen in the aromatic ring and in the side chains, etc.

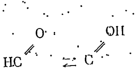
As was shown in Chapters III and IV, the mechanism of hydrogen isotope exchange is not fully understood, and it is probable that no single mechanism is common to all systems, but, irrespective of the intermediate stages of the exchange, the ability of tautomeric transformations to induce conjugated exchange has been convincingly proved. The relationship between anomalous exchange and tautomerism is so definite that one of the main methods for establishing tautomerism is by studying the number and structural positions of the exchanging atoms. This method has been used to prove the tautomerism of nitromethane [24] and of barbituric acid, represented by the equations

$$CH_3NO_2 \rightleftarrows CH_2 = NO_2OH \tag{8}$$



(9)

On the other hand, it has been shown by G. P. Miklukhin that the tautomerism assumed by some authors to exist in formic acid



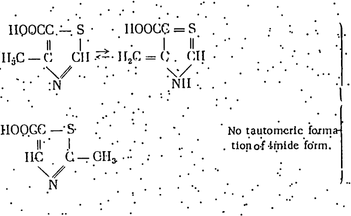
does not exist, since only one hydrogen atom in the molecule is isotopically exchanged with water [25]. Tautomerism represented by the equation

$$RCH_2NH_2 \rightleftharpoons RCH{=}NH_3 \tag{10}$$

does not occur in aliphatic amines [26].

Isotope methods have been used to show that tautomerism with formation of extranuclear double bonds is not involved in a series of reactions of the side chains of toluene and its derivatives (oxidation, nitration, halogenation) [27]. The results exclude the possibility not only of ordinary tautomerism, but of pseudomerism with the equilibria shifted to the limit. Important roles are attributed to pseudomeric forms in the mechanisms of many reactions; therefore the possibility of using isotopic exchange to verify the real existence of tautomeric transformations in compounds, and to study the characteristics of such transformations, makes the investigation of the number of H atoms involved in rapid exchange one of the most important methods for establishing the mechanisms of organic reactions.

A good illustration of the potentialities which this provides for explaining the relationship between fine distinctions in reactivity and chemical structure is given by the isotopic exchange of isomers of methylthiazole carboxylic acid [28] with heavy water. In presence of alkali the 4-methyl form rapidly exchanges 3 atoms of the methyl and 1 atom of the carboxyl group, and only the heterocyclic hydrogen is practically not exchanged. This is caused by the tautomeric transformation of the first isomer with appearance of imide hydrogen in the ring, and the absence of such transformation in the second isomer

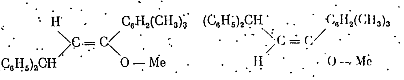


No tautomeric formation of imide form.

(11)

In an examination of the research on the role of tautomeric equilibria in the kinetics of isotopic exchange, some weak aspects must also be pointed out. As was noted earlier, recent work, largely by A. N. Nesmeyanov's school, has necessitated a revision of the fundamental positions of the classical theory of tautomerism. According to the latter, there is a direct connection between the ability of a substance to give rise to two series of derivatives, which are derivable from the isomeric formulas, and the existence of dynamic equilibrium isomerization in the Butlerov sense [29]. In other words, dual reactivity and tautomeric equilibrium are inextricably linked.

It has been shown by M. I. Kabachnik [30] that this view meets serious difficulties in the case of pseudomerism [31]. The latter is postulated if it is impossible to prove the existence of tautomeric equilibrium directly, and on the classical theory it is necessary to assume very strongly shifted equilibrium, with a high reactivity in the form present in negligible equilibrium concentration. Since both isomers consist of molecules of ordinary chemical structure, and not of free radicals or ions, their reactivities cannot conform to this hypothesis, this is not taken into consideration by some foreign authorities [32]. A. N. Nesmeyanov and his associates [14, 33] were the first to demonstrate, for metallic enolates of diphenylpropiomesitylene, which exist in cis- and trans-forms,



the possibility of dual reactivity, formerly regarded as characteristic of tautomers, in absence of a dynamic tautomeric equilibrium. This was clearly shown by the absence of cis- and trans-isomerization in conditions in which the reactions attributed to the two tautomeric forms occur fairly rapidly [33]. This effect proved to be fairly common, and it leads to the general important principle that the existence of equilibrium isomerism is not obligatory for dual reactivity [15]. Further development of these researches showed that even if such an equilibrium exists, ketonic derivatives are not always obtained from the keto-forms, or the enolic from the enolic forms. In many cases the cause is not tautomeric rearrangement at all, but special forms of conjugation of single and double bonds, while the reactions proceed by way of forms unusual in classical organic chemistry – free radicals and labile ions.

These new and unexpected relationships, discussed in detail by A. N. Nesmeyanov and M. I. Kabachnik [16], are not usually considered in investigations in which isotopic exchange is associated with tautomerism. The connection between these effects and protolytic equilibria also is not taken sufficiently into account. Nevertheless, the principal cases of tautomerism or of effects attributed to it reduce to hydrogen transfer with simultaneous migration of multiple bonds. For this reason, results obtained by means of isotopic exchange as a method for the detection of tautomerism must be treated with caution. Probably only negative results are conclusive. At the same time, isotope methods may also assist in elucidating the nature of dual reactivity.

This situation creates the need for checking earlier investigations with the aid of new facts and concepts. A very important part of such work is to obtain additional data on the rates of deuterium exchange and of the numbers of hydrogen atoms involved in it, by investigations of kinetic isotope effects.

§ . The Kinetic Additivity of Complicated Isotopic Exchange

In isotopic exchange kinetics complicated by the presence of several or many species, a question of fundamental importance is whether the kinetic orders and kinetic constants (E_i, k_{0i}, etc.) which characterize the isotopic exchange of the individual species change, or not, if several isotopic exchange reactions occur simultaneously.

We shall describe exchange in systems of the first type as additive, additivity being taken to mean the retention in unchanged form of each of the individual processes, which can be summated according to the rules and laws used in the kinetics of parallel chemical reactions. Since all the individual processes are reversible and may have greatly different kinetic coefficients, such summation may lead to conjugated or induced reactions, catalytic transfer, and other types of complex kinetics; but each term in the sum has the same character as in the analogous isotopic exchange reaction in a simple system.

Exchange in systems of the second type will be described as nonadditive. In such cases the equation and coefficients which represent the individual processes in simple systems are not applicable to some or all of these processes in complicated conditions.

Most kinetic investigations of complex reactions are based on the explicit assumption that the experimentally observed deviations from additivity are always apparent, and that if all the individual processes are taken into account all systems are kinetically additive (in the sense of the term as defined above). The general applicability of this assumption to elementary chemical reactions is not evident, although it is very wide. For isotopic exchange it can be regarded as valid in all cases, as some of the complicating factors which can cause deviations from additivity are absent. Therefore, in principle, the derivation of kinetic equations for isotope exchange in systems of any degree of complexity reduces to compilation of a system of differential equations, each of which characterizes the rate of an individual exchange reaction, and the simultaneous solution of the system of equations so obtained. In practice, if numerous individual reactions occur simultaneously, complete solutions are of little value because of their complexity and lack of clarity. The usual aim is therefore to choose experimental conditions in which some individual reactions can be neglected.

As will be shown below, in the case of fairly complex systems another statistical approach is possible, which greatly simplifies the final mathematical relationships. We will use this general method, which has been recently developed, for the more complex cases.

§ 6. Kinetics in Presence of Two Independent Acceptors

Serious complications in the kinetics of isotopic exchange can be caused even by the presence, in the molecules of any of the exchanging substances, of two X atoms with different exchange reactivities owing to differences in their structural positions.

Let us consider the isotopic exchange of a molecule AX_2 with molecules $B\overset{*}{X}$ if two X atoms in the first molecule are present in different structural positions α and β:

$$AX^{\alpha}X^{\beta} + B\overset{*}{X} \begin{cases} \xrightarrow[k_{\alpha}]{(a)} A\overset{*}{X}{}^{\alpha}X^{\beta} + BX \\ \xrightarrow[k_{\beta}]{(b)} AX^{\alpha}\overset{*}{X}{}^{\beta} + BX \end{cases} \qquad (12)$$

We assume that there is no direct intramolecular or intermolecular exchange between X^{α} and X^{β} atoms, and that their only mutual influence in exchange is due to reversibility of the Reactions (12a) and (12b), so that they can be transferred through a common donor.

To the designations in Chapter II we add the following: we represent the concentrations of the molecules containing the radioactive atoms $\overset{*}{X}{}^{\alpha}$ and $\overset{*}{X}{}^{\beta}$, by $[\overset{*}{A}_{\alpha}] = [A\overset{*}{X}{}^{\alpha}X^{\beta}] + [A\overset{*}{X}{}^{\alpha}\overset{*}{X}{}^{\beta}]$; $[\overset{*}{A}_{\beta}] = [AX^{\alpha}\overset{*}{X}{}^{\beta}] + [A\overset{*}{X}{}^{\alpha}\overset{*}{X}{}^{\beta}]$; and we note that in this case $[A] = [AX^{\alpha}X^{\beta}] + [A\overset{*}{X}{}^{\alpha}X^{\beta}] + [AX^{\alpha}\overset{*}{X}{}^{\beta}] + [A\overset{*}{X}{}^{\alpha}\overset{*}{X}{}^{\beta}]$. If at the start of the experiment when $t = 0$ $[\overset{*}{A}_{\alpha}] = 0$ and $[\overset{*}{A}_{\beta}] = 0$, the exchange fraction F at time t, can be written as

$$F = \frac{[\overset{*}{A}_{\alpha}] + [\overset{*}{A}_{\beta}]}{[\overset{*}{B}] \cdot \frac{[A]}{[A]+[B]}} \qquad (13)$$

The differential equations for the rates of increase of $[\overset{*}{A}_{\alpha}]$ and $[\overset{*}{A}_{\beta}]$ take the form

$$\left.\begin{aligned} &a)\ \frac{d[\overset{*}{A}_{\alpha}]}{dt} = \frac{[\overset{*}{B}]}{[B]}R_{\alpha} - \frac{[\overset{*}{A}_{\alpha}]}{[A]/2}R_{\alpha};\\ &b)\ \frac{d[\overset{*}{A}_{\beta}]}{dt} = \frac{[\overset{*}{B}]}{[B]}R_{\beta} - \frac{[A_{\beta}]}{[A]/2}R_{\beta}, \end{aligned}\right\} \qquad (14)$$

where R_{α} is the total rate of Reaction (12a) and R_{β} is the total rate of Reaction (12b).

As was pointed out earlier, the value of $[\overset{*}{B}]$ is connected both with $[\overset{*}{A}_{\alpha}]$, and with $[\overset{*}{A}_{\beta}]$ by the corresponding kinetic equations and isotopic exchange equilibrium constants; therefore the complete solution of Eq. (14) is complex and lacks clarity. The position is simplified in some limiting cases. We are most interested in one of these, in which the concentration of tagged molecules $[\overset{*}{B}]$ and the corresponding fractional content ρ_{β}^{*} remain practically unchanged during the experiment. This may occur with a very high excess of B in the system

$$[B] \gg [A], \qquad (15)$$

and therefore

$$[\overset{*}{B}] \approx \text{const} \approx [\overset{*}{B}_{\infty}], \qquad (15a)$$

and also if BX and $B\overset{*}{X}$ are continuously added during the process, for example, if the stream of tagged BX flows at an excess rate in heterogeneous exchange of a solid surface in a stream.

In both cases:

$$\rho = \rho_{A_{\infty}} = \rho_{A_{\alpha\infty}} = \rho_{A_{\beta\infty}} = \rho_{B\infty} \approx \rho_{B_0} \approx \rho_{B} \qquad (15b)$$

And in the Eqs. (14)

$$\frac{[\overset{*}{B}]}{[B]} = \rho_{B} = \text{const} \qquad (14a)$$

In these conditions each of the Eqs. (14) can be integrated separately; the following expressions being obtained for $\rho_{A_{\alpha}}^{(t)}$ and $\rho_{A_{\beta}}^{(t)}$:

$$\left.\begin{aligned} &a)\ \rho_{A_{\alpha}} = 0.5\,\rho_{\beta}\,[1 - e^{\frac{-2R_{\alpha}t}{[A]}}] = 0.5\rho\,[1 - e^{\frac{-2R_{\alpha}t}{[A]}}],\\ &b)\ \rho_{A_{\beta}} = 0.5\,\rho_{\beta}\,[1 - e^{\frac{-2R_{\beta}t}{[A]}}] = 0.5\rho\,[1 - e^{\frac{2R_{\beta}t}{[A]}}]. \end{aligned}\right\} \qquad (16)$$

It is evident that the exchange of each of the atoms X^α and X^β in the molecule is strictly exponential, i. e.,

$$\left.\begin{aligned} a)\ \frac{d\rho_\alpha}{dt} &= -\frac{\rho R_\alpha}{[A]}\, e^{-\frac{2R_\alpha t}{[A]}}; \\ b)\ \frac{d\rho_\beta}{dt} &= -\frac{\rho R_\beta}{[A]}\, e^{-\frac{2R_\beta t}{[A]}}. \end{aligned}\right\} \qquad (17)$$

By putting $F_\alpha = \frac{[\overset{*}{A}_\alpha]}{[\overset{*}{A}_{\alpha\infty}]}$ and $F_\beta = \frac{[\overset{*}{A}_\beta]}{[\overset{*}{A}_{\beta\infty}]}$ and replacing the denominators by $[A][\overset{*}{B}]/[B]$, we can write.

$$\left.\begin{aligned} a)\ F_\alpha &= \frac{[\overset{*}{A}_\alpha][B]}{[A][\overset{*}{B}]} = 1 - e^{-\frac{2R_\alpha t}{[A]}}; \\ b)\ F_\beta &= \frac{[\overset{*}{A}_\beta][B]}{[A][\overset{*}{B}]} = 1 - e^{-\frac{2R_\beta t}{[A]}}. \end{aligned}\right\} \qquad (18)$$

Let us also find how $F = \frac{1}{2}\,[F_\alpha + F_\beta]$ varies with time. Summation of (18a) with (18b) give (19)

$$F = \frac{\{[\overset{*}{A}_\alpha] + [\overset{*}{A}_\beta]\}[B]}{[\overset{*}{B}][A]} = 1 - \left[\frac{e^{-\frac{3R_\alpha t}{[A]}} + e^{-\frac{2R_\beta t}{[A]}}}{2}\right] \qquad (19)$$

F is no longer exponential.

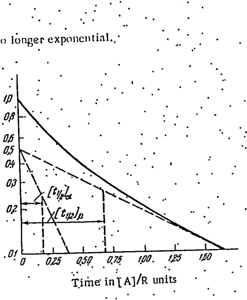


Fig. 73. Theoretical logarithmic plot for the complicated exchange reactions

$$B\overset{*}{X} + AX^\alpha X^\beta \overset{R_\alpha}{=} BX + A\overset{*}{X}{}^\alpha X^\beta,$$
$$B\overset{*}{X} + AX^\alpha X^\beta \overset{R_\beta}{=} BX + AX^\alpha \overset{*}{X}{}^\beta$$

R_α and R_β are the rates of exchange of $\overset{*}{X}$ atoms in $B\overset{*}{X}$ with X^α and X^β, respectively. The continuous line represents the complicated exchange curve; the broken lines represent the components obtained by resolution of the complicated exchange curve.

If sufficient points in the initial and final portions of the $(1-F) = f(t)$ exchange curves (Fig. 73) are available, it is possible to identify linear regions and to determine $t_{1/2}$, R_α and R_β from their slopes.

For simple isotopic exchange

$$R = \frac{[A][B]}{[A]+[B]}\,\frac{0.693}{\tau_{1/2}}, \qquad (20)$$

and for the present instance of the simplest case of complicated exchange

$$R_\alpha = \frac{[A]}{2}\cdot\frac{0.693}{(t_{1/2})_\alpha} \qquad (21)$$

and

$$R_\beta = \frac{[A]}{2}\cdot\frac{0.693}{(t_{1/2})_\beta}. \qquad (22)$$

In cases in which the Inequality (15) is not satisfied and the decrease of [B] caused by isotopic exchange is not restored, the more rapidly exchanging atoms, because of the reversibility of isotopic exchange, begin to act as intermediate labile products with respect to the exchange of slowly exchanging atoms; this leads to peculiar kinetic anomalies which play a significant role in the kinetic and catalytic applications of isotopic methods.

In illustration, we shall consider the nature of these anomalies in the exchange of $AX^\alpha X^\beta$ molecules when

$$R_\alpha \gg R_\beta. \qquad (23)$$

First, a certain quasi-stationary distribution of isotope $\overset{*}{X}$ between BX and X^α atoms in $AX^\alpha X^\beta$ will be rapidly attained. The kinetics of this step will be increasingly near to simple exponentiality for higher values of the ratio R_α/R_β. In the particular case when $[B] \ll [A]$, and the Inequality (23) is obeyed, the quasi-stationary distribution will be

$$[\overset{*}{A}_\alpha]_{quasist} = [\overset{*}{B}]_{quasist} = 2[\overset{*}{A}_\alpha]_{equil} = 2[\overset{*}{A}_\beta]_{equil} = 2[\overset{*}{B}]_{equil}. \qquad (24)$$

This quasi-equilibrium corresponds to true equilibrium in simple exchange of molecules containing one X atom each, i. e., $AX + B\overset{*}{X}$. The constant R for this exchange, for our case of complicated exchange, is R_α, and $[\overset{*}{A}_\alpha]_{quasist} = [\overset{*}{A}]_\infty$ where $[\overset{*}{A}]_\infty$ is the equilibrium final concentration of $A\overset{*}{X}$ molecules in simple exchange. $[\overset{*}{A}]_\infty$ in this equation is double $[\overset{*}{A}]_{equil}$; i. e., double the value of $[\overset{*}{A}]_\infty$ in Eq. (24), which applies to the exchange of AX_2 molecules.

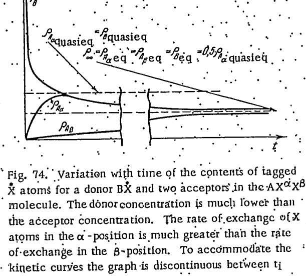


Fig. 74. Variation with time of the contents of tagged $\overset{*}{X}$ atoms for a donor $B\overset{*}{X}$ and two acceptors in the $AX^\alpha X^\beta$ molecule. The donor concentration is much lower than the acceptor concentration. The rate of exchange of X atoms in the α-position is much greater than the rate of exchange in the β-position. To accommodate the kinetic curves the graph is discontinuous between t_i and t_j; $t_i \ll t_j$.

When isotopic quasi-equilibrium between $B\overset{*}{X}$ and X_α atoms in AX_2 molecules has been reached, because $[B] \ll [A]$, most of the isotope $\overset{*}{X}$ will be concentrated in these molecules. Therefore it is approximately true that subsequently the process for AX reduces to redistribution of $\overset{*}{X}$ between the positions X^α and X^β through the agency of $B\overset{*}{X}$ which acts as a carrier. The content of $\overset{*}{X}$ in the α-position will fall continuously from $[\overset{*}{A}_\alpha]_{quasist}$ to $[\overset{*}{A}_\alpha]_{stat} = 0.5\,[\overset{*}{A}_\alpha]_{quasist}$. $[\overset{*}{A}_\beta]$ will tend to the same value from the time when the quasi-stationary distribution has been attained for $[\overset{*}{A}_\alpha]$, when $[\overset{*}{A}_\beta]$ is close to zero. The decrease of ρ_{A_α} and the increase of ρ_{A_β} will be practically exponential with $R \approx R_\beta$.

The decrease of the values of $[\overset{*}{B}]$ and $\rho_{\overset{*}{B}}$ from the quasi-stationary to the equilibrium states will follow the same law, with the same R, and.

$$\left.\begin{aligned} [\overset{*}{B}]_{equil} &\approx 0.5\,[\overset{*}{B}]_{quasist}, \\ \rho_{B_{equil}} &\approx 0.5\,\rho_{B_{quasist}}. \end{aligned}\right\} \qquad (25)$$

These relationships are represented in Fig. 74. By the condition $[B] \ll [A]$, very simple numerical relationships exist between the concentrations and the values of ρ of the tagged molecules at the end of the first rapid stage and after true equilibrium has been reached. The same type of kinetic curves, but with different numerical relationships between the values for the quasi-stationary and equilibrium states, will be obtained for other ratios of [B] to [A].

As the values of R_α and R_β come closer together, the qualitative picture remains the same. In particular, the values of ρ_{A_α} will still pass through a maximum, but the simple exponential character of the individual curves, or of the ascending and descending branches of the curve with the maximum, which we emphasized in the examination of the limiting case, will disappear. It must be remembered that, in general, both R_α and R_β contain in implicit form the exponents $\exp(-E/RT)$ with different values of E. Because of this, the magnitude of the ratio R_α/R_β can be varied within wide limits by variations of the experimental temperature.

In the foregoing we dealt mainly with the existence of two types of distribution of the isotope $\overset{*}{X}$: quasi-stationary and true equilibrium, and with the appearance of maxima for $[\overset{*}{A}_{\alpha}]$ and $\rho_{A^{\alpha}}$. Myers and Prestwood [2] have given the kinetic derivation of the variation of F with time, and certain other relationships which augment our discussion of the exchange of AX_2 with BX when $R_{\alpha} \gg R_{\beta}$.

All the above refers to the exchange of molecules each containing one atom of a definite isotope in two different states. An increase of the number of X atoms in the α- and β-positions by passing to molecules of $AX_n^{\alpha}X_m^{\beta}$ introduces nothing new in principle. But instead of the coefficient 2, the corresponding equations will contain the coefficients $\frac{n+m}{n}$ and $\frac{m+n}{m}$.

Thus, in the exchange of $B\overset{*}{X}$ with molecules of $AX_n^{\alpha}X_m^{\beta}$, on the above assumptions concerning the ratios $\frac{[B]}{[A]}$ and $\frac{R_{\alpha}}{R_{\beta}}$, $[\overset{*}{A}_{\alpha}]_{quasist}$ will be $\frac{m+n}{n}$ times as large as $[\overset{*}{A}]_{equil}$. In particular, when n = 1 and m = 5, the specific activity at the maximum will be nearly 6 times the equilibrium value, while when n = 5 and m = 1 it will exceed the equilibrium value by only 1/5.

The existence of element X in more than two states in molecules such as $AX_n^{\alpha}X_m^{\beta}X_p^{\gamma}$, etc., where n + m + p = s, and the presence of two or more types of X atoms in the donor molecules $B\overset{*}{X}_y$, makes possible the occurrence of $\rho_i(t)$ curves with maxima for several p_i, and also the appearance of minima on some of them.* This is illustrated in Fig. 75. In the first case the total concentration $[B]_0$ of the donors $B\overset{*}{X}_y$ is much higher than the concentration $[A]_0$ of AX_s, with three forms of X present in AX_s and two forms of $\overset{*}{X}$ in $B\overset{*}{X}_y$. The presence of two forms of $\overset{*}{X}$ in $B\overset{*}{X}_y$ only affects the magnitude of the exchange rate constants. ρ_B for $B\overset{*}{X}$ as a whole and ρ_{B^i} and ρ_{B^j} for the two forms of X remain practically the same the whole time, and therefore $\rho \approx \rho_B = \rho_{B^i} = \rho_{B^j}$. A separate straight line is obtained in $\ln(\rho - \rho_A)$, t or $\ln(1 - \overset{*}{F}_A)$, t coordinates for each type of X atoms in AX_n (Fig. 75a). In ρ_A, t coordinates this corresponds to three first-order kinetic curves with different values of R (Fig. 75b). It is assumed in both figures that $R_{\alpha} : R_{\gamma} : R_{\beta} = 12 : 3 : 2$. Because ρ_B is constant, the exchange of all the types of X occurs practically independently and strictly by a first order law without maxima or minima.

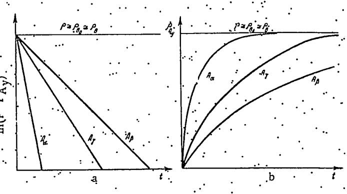


Fig. 75. Exchange of $AX_n^{\alpha}X_m^{\beta}X_p^{\gamma}$ with $B\overset{*}{X}{}_b^i\overset{*}{X}{}_d^j$ when $[B_0] \gg [A_0]$ and $R_{\alpha} > R_{\gamma} > R_{\beta}$. a) Kinetic curves in $\ln(\rho - \rho_{A_y})$ and (− t) coordinates; b) kinetic curves in ρ and t coordinates. The curves A_{α}, A_{β}, A_{γ} represent the exchange of different types of atoms, X^{α}, X^{β}, and X^{γ} in the compound $AX_n^{\alpha}X_m^{\beta}X_p^{\gamma}$.

The situation changes sharply at low relative concentrations of B. Figure 76a represents the course of exchange of $AX_n^{\alpha}X_m^{\beta}$ with $BX_b^iX_d^j$ for $[B_0] = 0.25\,[A_0]$, the number of rapidly exchanging X^i atoms in $BX_b^iX_d^j$, where b + d = y, is 4 times the number of slowly exchanging X^j atoms (b = 4d). In AX_s molecules X^s atoms exchange much more rapidly than X^{β} atoms both with X^i and with X^j. The first curve, with an initial minimum and a very flat maximum in the middle represents the course of ρ_{B^i} when $R_{\alpha} \gg R_{\beta}$. The content of X^i falls steeply to values close to equipartition, with X^j atoms in $B\overset{*}{X}{}_b^i\overset{*}{X}{}_d^j$ and X^{β} atoms in $AX_n^{\alpha}X_m^{\beta}$ not participating in the exchange at all. The value of $\rho_{A_{\alpha}}$ increases and tends to the same value of $\rho_{B^i quasieq\,1}$. Here ρ_{B^i} is 66% of ρ_{B_0} and $\rho_{A_{\beta}}$ is practically zero. Subsequently, because of the participation of X^j atoms in exchange with X^{α}, and of the reversibility of the exchange of $\overset{*}{X}{}^i$ atoms with X^{α}, ρ_{B^i} and $\rho_{A^{\alpha}}$ will increase and tend to a new value $\rho_{B^i quasieq}$ which corresponds to the exchange of all X from $B\overset{*}{X}{}_b^iX_d^j$ molecules with X^{α} atoms in $AX_n^{\alpha}X_m^{\beta}$ molecules. ρ_{B^j} tends to the same value. Finally, true equilibrium distribution involving all types of X atoms, represented by a broken line, will be reached still more slowly. ρ_{B^i} passes through a minimum and a maximum, $\rho_{A_{\alpha}}$ passes through a flat maximum, and only $\rho_{A_{\beta}}$ increases smoothly, but very slowly, tending to a true equilibrium value.

---

* We put $B\overset{*}{X}_y$ for molecules containing at least one $\overset{*}{X}$ atom.

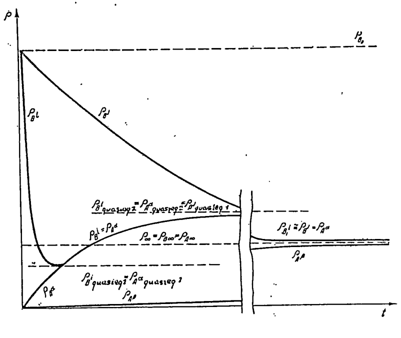


Fig. 76a. Kinetics of the exchange of a tagged donor $B\overset{*}{X}{}_b^i\overset{*}{X}{}_d^j$ with an acceptor $AX_n^{\alpha}X_m^{\beta}$; $w_{\overset{*}{X}^i, A} \gg w_{\overset{*}{X}^j, A}$; $w_{X^{\beta}, \overset{*}{X}^i} \ll w_{X^{\beta}, \overset{*}{X}^j}$; $w_{X^{\alpha}, \overset{*}{X}} \gg w_{X^{\beta}, \overset{*}{X}}$.

Figure 76b represents exchange with a different relationship between the individual rates R. As before exchange of X^{α} with $\overset{*}{X}{}^i$ is the most rapid, but in this instance the rate of exchange of X^{β} with X^i is greater than the rate of exchange of X^{α} with X^j. Therefore, when the value $\rho_{A_{\alpha} quasieq\,1} = \rho_{B^i quasieq\,1}$ has been reached, these two quantities will continue to decrease, slowly tending to the new value $\rho_{A\alpha quasieq\,2} = \rho_{A_{\beta} quasieq\,1} = \rho_{B^i quasieq\,2}$. The further increase of $\rho_{A_{\alpha}}$, $\rho_{A_{\beta}}$, and ρ_{B^i}, due to inclusion of X^j atoms in the process, will occur still more slowly. As a result, the $\rho_{A_{\alpha}}$ curve will have a maximum and a minimum, the ρ_{B^i} curve will have a minimum, $\rho_{A_{\beta}}$ will increase continuously, and ρ_{B^j} will decrease continuously. Additional maxima and minima may appear if the multiple substitution occurs in stages.

The exchange of $B\overset{*}{X}$ molecules with a mixture containing two or more kinds of molecules A_1X, A_2X, A_3X, etc., in absence of subsidiary exchange processes between the acceptors, and assuming additivity of the isotopic exchange, can be reduced from the kinetic standpoint to the type discussed above. The main distinction between complicated exchange with a mixutre of molecules and complicated exchange with molecules containing two or more types of X atoms lies in the possibility of varying, in any desired limits, the ratio of A_1X to A_2X, to A_3X, etc., while the ratio $(X^{\alpha}) : (X^{\beta}) : (X^{\gamma})$ can be varied only within narrow limits, and consists of the ratio of small whole numbers. Thus, for the simplest case of exchange of $B\overset{*}{X}$ with a molecule $AX^{\alpha}X^{\beta}$ $n_{X^{\alpha}} : n_{X^{\beta}} = 1$, while in the analogous exchange of a mixture $A_1X + A_2X$ with $B\overset{*}{X}$ the ratio $n_{A_1X} : n_{A_2X}$ can vary from ∞ to 0 for different compositions of the mixture. Even in more complex molecules of the type $AX_m^{\alpha}X_n^{\beta}X_p^{\gamma}X_r^{\delta}$ the ratio of extreme values of m, n, p, and r usually does not exceed 10. For example, the molecule of cinnamic acid $C_9O_2H_8$


$C_6H_5-CH=CHCOOH$

contains six types of hydrogen atoms: one carboxylic atom, one attached to carbon in the side chain in the α-position to —COOH, one at the carbon atom linked to the phenyl, one in the para-position in the phenyl radical, and two each in the ortho- and meta-positions. Thus, there are six coefficients, m, n, etc., but they are all either 1 or 2

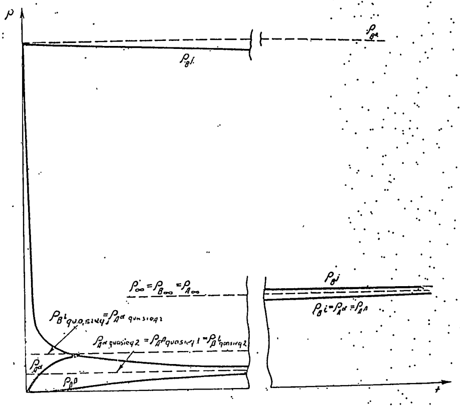


Fig. 76b. Kinetics of the exchange of a tagged donor $BX_b^iX_d^j$ with an acceptor $AX_n^\alpha X_m^\beta$; $n = m$; $d \gg b$; $[B] < [A]$; $w_{X^\alpha,\overset{*}{X}^i} \gg w_{X^\beta;\overset{*}{X}^i}$; $w_{X^\beta,\overset{*}{X}^i} \gg w_{X^\alpha;\overset{*}{X}^j}$.

For tertiary butyl alcohol $(CH_3)_3(COH)$ the ratio is greater: there are 9 methyl group H atoms to one atom in the alcohol hydroxyl; but in general, m, n, etc. are of similar magnitude. Exceptions are possible only for very large molecules of complex structure, such as molecules of natural and synthetic polymers.

It may seem at first sight that an increase of the number of exchanging atoms in a molecule should not in itself lead to significant kinetic complications. From this point of view, transition from methyl chloride CH_3Cl with one chlorine atom in the molecule to carbon tetrachloride CCl_4 with four identical chlorine atoms should introduce nothing new in principle into exchange with Cl^- ions or Cl atoms. Similarly, it is natural to consider that the isotopic exchange of protium in the cyclohexane molecule, containing 12 hydrogen atoms in identical positions, with deuterium in DCl, is similar to exchange between DCl and AH molecules containing only one hydrogen atom each. This is true for a simple bimolecular mechanism in the exchange of molecules containing two or more atoms of the exchanging isotope, with a low initial content of one of the isotopes in both exchanging molecules. In this case only the limit to which the system tends at equipartition changes, and the rates of particular stages are multiplied by the appropriate factors because of several equivalent exchange possibilities. For example, in the process

$$C_6H_{12} + DCl \rightarrow C_6H_{11}D + HCl \qquad (26)$$

the rate of the single reaction must be multiplied by 12, as each of the 12 atoms in hexamethylene can enter the process with equal probability. Serious complications, affecting the isotopic composition of the reaction products, may occur in the exchange of AX_n with $B\overset{*}{X}$ if the exchange proceeds through intermediate active forms

with higher exchange reactivity. Suppose that the biradical $—C_6H_{12}—$, i. e., $—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—$, formed by ring cleavage persists for a time which is considerably greater than the average period of thermal vibrations, $\sim 10^{-12}$ second, and that hydrogen is exchanged considerably more rapidly in this radical than in saturated C_6H_{12} molecules. Then it may happen in exchange with completely deuterated compounds such as water, sulfuric acid, etc., that practically only the biradicals will exchange and that, having once been formed, a biradical will have time to exchange all its hydrogen before it returns to the inert state of saturated cyclohexane. Under such conditions C_6D_{12} molecules will be formed at the rate of generation of the biradicals, which is equal to the rate of their disappearance by ring closure; while molecules with low contents of D will be formed at other considerably lower rates.

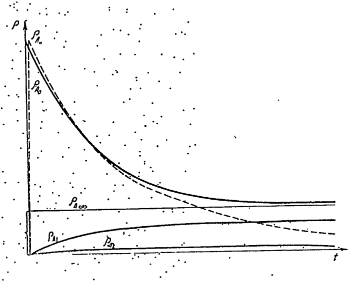


Fig. 77a. Variation of the specific content of a tagged isotope $\overset{*}{X}$ with time in molecules of $AX_{n-i}\overset{*}{X}_i$ at i = 0, i = 1, i = 2; and i = n, at $t_{1/2} > \tau_{1/2}$; $t_{1/2}$ is the half-conversion time by the reaction $A\overset{*}{X}_n + AX_n \rightarrow A\overset{*}{X}_{n-1}X + AX_{n-1}\overset{*}{X}$; $\tau_{1/2}$ is the exchange time in the radical.

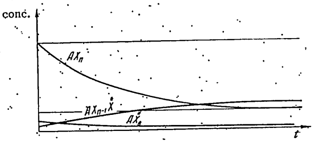


Fig. 77b. Variation of the concentrations of AX_n, $A\overset{*}{X}_n$, $AX_{n-1}\overset{*}{X}$ with the exchange time.

In other words, instead of the simple initial formation of monosubstituted molecules, followed by di- tri- and polysubstituted molecules, the situation represented in Figs. 77a and 77b may arise. It must be pointed out that every di- and polysubstituted molecule is in reality formed by way of a monosubstituted molecule, but the number of active molecules capable of substitution is so small that the system first reaches quasi-equilibrium, at which the fraction of polysubstituted molecules exceeds the possible value for true equilibrium. In the ordinary exchange mechanism without participation of active forms the same type of variation of the isotopic composition with time for the exchange of AX_n with $B\overset{*}{X}$ when $n_X \gg n_{\overset{*}{X}}$ may be obtained by carrying out the exchange by portions; for example, by first adding to the mixture together with the isotopically pure donor $B\overset{*}{X}$, a very small quantity of AX_n, and only after equilibrium has been reached, corresponding to

$$n_X \ll n_{\overset{*}{X}}, \tag{27}$$

when

$$[A\overset{*}{X}_n] > [AX_{n-1}\overset{*}{X}] \cdots [A\overset{*}{X}X_{n-1}] > (AX_n), \tag{28}$$

adding an additional portion of AX_n to the system, to equalize n_X and $n_{\overset{*}{X}}$ in the system

$$n_X \approx n_{\overset{*}{X}}$$

With this composition new equilibrium will become established in the system after some time, with predominance of $A\overset{*}{X}_{n-2}X_{n-2}$ tagged molecules. By adding a third portion, which makes n_X predominant in the system, after some time a third equilibrium state may be reached in the system, with AX_n predominant, and with $A\overset{*}{X}X_{n-1}$ predominant among the tagged molecules.

In an actual single experiment with exchange effected by active particles, the system passes through quasi-equilibria instead of true equilibria, and not in three steps but continuously through all the intermediate stages. Let us consider this question in somewhat greater detail, using the same graphical method. We commence with the case in which the isotope donor BX is present in large excess and consists almost entirely of $B\overset{*}{X}$ molecules. Then

$$\rho_B(t) \approx \rho_{B_\infty} \approx \rho_{B_0} = 1,$$

and the AX_n molecules tend to the same p_∞.

In simple consecutive exchange with equal equilibrium constants $k_1, k_2, \ldots k_i$ for the substitution of the first of all subsequent X atoms,* molecules of $AX_{n-1}\overset{*}{X}$ should appear first.

As their concentration increases, the formation of $AX_{n-2}\overset{*}{X}_2$ molecules becomes appreciable, followed by $AX_{n-3}\overset{*}{X}_3$, etc. Of all the concentrations, only $[A\overset{*}{X}_n]$ will increase continuously, tending to $[A\overset{*}{X}_n]_\infty = [AX_n] = A$, and only $[AX_n]$ will decrease continuously, tending to zero. The absolute concentrations and specific contents of all the other substitution products $AX_{n-1}\overset{*}{X}$ will pass through maxima, the time t_{m_i} in which they are reached increasing with the number of $\overset{*}{X}$ atoms in the molecule. The exact form of the curves can be easily determined by a method analogous to that used in the theory of the radioactive disintegration series. With the assumption that $[B] \gg [A]$ and that all the n atoms in the molecule are substituted strictly consecutively and independently, we have a sequence of conversions each of which is of the first order. We shall not take into account changes in the reactivity of X atoms caused by replacement of some of them by $\overset{*}{X}$ atoms, and we shall assume that the formation of $AX_{n-i}\overset{*}{X}_i$ molecules occurs only by the interaction of $AX_{n-i+1}\overset{*}{X}_{i-1}$ molecules with $B\overset{*}{X}$.

With our assumptions, the reverse reactions may be ignored, and each stage and the exchange process as a whole are regarded as practically irreversible. If we assume that the reaction of each X atom in the $AX_{n-i}X_i$ molecules with $B\overset{*}{X}$ is equally probable, we obtain a regularly decreasing series of exchange rate constants: nk; (n−1)k; to k inclusive, and a series of differential equations:

$$\left.\begin{array}{ll}
\text{a)} & -\dfrac{dA_0}{dt} = nk\,A_0 = r_0 \cdot A_0; \\
\text{b)} & -\dfrac{dA_1}{dt} = (n-1)\,k\,A_1B - r_0A_0 = r_1A_0 - r_0A_0; \\
\text{c)} & -\dfrac{dA_2}{dt} = r_2A_2 - r_1A_1; \\
 & \cdots\cdots\cdots\cdots\cdots\cdots \\
\text{d)} & -\dfrac{dA_n}{dt} = -r_{n-1}A_{n-1},
\end{array}\right\} \tag{30}$$

where $r_1 = (n-1)k \cdot B$; B is the concentration of $B\overset{*}{X}$ and $A_0, A_1, A_2 \ldots$ are the concentrations of AX_n, $AX_{n-1}\overset{*}{X}$, $AX_{n-2}\overset{*}{X}_r \ldots$; A is the total concentration of molecules of $A = A_0 + A_1 + A_i + \ldots$. We assume for simplicity that at the initial instant only AX_n and $B\overset{*}{X}$ molecules are present, and therefore at $t = 0$

$$A_{01} = A_{02} \ldots = A_{0n} = 0. \tag{30a}$$

Of the n types of AX_n molecules involved in the processes represented by the Eqs. (30), we distinguish two from the kinetic standpoint: 1) molecules of AX_n the concentration of which falls continuously according to the exponential equation

$$A_0 = Ae^{r_0t}, \tag{31}$$

which is easily obtained by integration of Eq. (30a); 2) molecules of $A\overset{*}{X}_n$, the concentration of which rises from zero to A (see Fig. 77b). The concentrations of all the intermediate isotopic substitution products, A_1, A_2, etc., pass through maxima. Here we give the solution for the concentration of monosubstituted molecules A_1. From Eqs. (30b) and (31)

$$\frac{dA_1}{dt} = r_0A_0 - r_1A_1 = r_0Ae^{-r_0t} - r_1A_1 \tag{32}$$

This is a linear differential equation of the first order, which may be solved according to the usual methods [35] in the form

$$A_1 = \frac{r_0A}{r_1 - r_0}e^{-r_0t} + Ie^{-r_1t}, \tag{32a}$$

where I is the integration constant.

In this instance $r_0 = nkB$ and $r_1 = (n-1)kB$. Substituting these into the fraction in the first term, we have:

$$A_1 = -nAe^{-r_0t} + Ie^{-r_1t} \tag{32b}$$

From the initial conditions I is readily found to be

$$I = nA. \tag{32c}$$

In this final form the relationship $A_1 = A_1(t)$ is represented by Eq. (32d), written in three forms

$$\left.\begin{array}{ll}
1) & A_1 = \dfrac{Ar_0}{r_1 - r_0}(e^{-r_0t} - e^{-r_1t}); \\
2) & A_1 = -nA\,(e^{-r_0t} - e^{-r_1t}); \\
3) & A_1 = nA \cdot e^{-r_1t}(1 - e^{-k_1t}).
\end{array}\right\} \tag{32d}$$

In this equation $k_1 = kB$. Eq. (32d) is the complete analog of the equations used in the theory of radioactive families for changes of the first radioactive product with time. Here r_0 is analogous to λ_1, r_1 is analogous to λ_2 and A is analogous to N_{10} [36, 37]. This analogy extends to all the subsequent substitution products while retaining some definite characteristics:*

1. r_0, r_1, etc. are not conversion rate constants in the ordinary sense, but contain a concentration factor B in implicit form.

2. The constants r decrease regularly from nkB to kB, passing through all intermediate values. For a radioactive family this would correspond to values of λ_i decreasing according to the same law.

---

* The rate constant k refers to one atom. This, like R, is a constant value, unlike nk, which is referred to one molecule.

* $\lambda_1, \lambda_2, \lambda_3, \ldots$ are the rate constants for radioactive disintegration of the first, second, ith member of a radioactive family; N_1, N_2, etc. are the numbers of atoms of the first and subsequent members of the radioactive family; N_{10}, N_{20}, etc. are their initial numbers.

3. In contrast to radioactive families, in which the final stable product is usually of no interest, the law for the formation of the final, unchanging product in the isotopic substitution series is of great interest.

4. The substitution is reversible in principle.

5. All the r depend on the temperature.

Despite this, by analogy with radioactive disintegration, it is possible to use in final form the equations for the 3rd and ith intermediate substitution products, taking into account the special characteristics of the rate constants r. Evidently this can only be done if the initial conditions are maintained, but a sufficiently close approach to these conditions can be made by appropriate experimental procedure.

For the second member of a radioactive series, when $N_{20} = 0$ and $N_{30} = 0$, the expression $N_3 = N_3(t)$ takes the form

$$N_3 = \lambda_1 \cdot \lambda_3 N_{10}\left[\frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} + \frac{e^{-\lambda_2 t}}{(\lambda_3 - \lambda_2)(\lambda_1 - \lambda_2)} + \frac{e^{-\lambda_3 t}}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)}\right] \tag{33}$$

For disintegration which commences at zero concentrations of the products, the expression for the ith member of the series is

$$N_i = \lambda_1 \cdot \lambda_2 \cdots \lambda_{i-1} N_{10}\left[\frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)\cdots(\lambda_i - \lambda_1)} + \frac{e^{-\lambda_2 t}}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)\cdots(\lambda_i - \lambda_2)} + \cdots + \frac{e^{-\lambda_n t}}{(\lambda_1 - \lambda_n)\cdots(\lambda_{i-1} - \lambda_n)}\right] \tag{33a}$$

Putting r for λ, shifting the subscripts back by 1 unit, and replacing N_{10} by A_0, remembering that

$$r_0 : r_1 : r_2 : \cdots r_{n-1} = n : (n-1) : (n-2) : \cdots : 1, \tag{34}$$

and consequently,

$$r_i - r_{i-1} = k_1, \tag{34a}$$

we obtain

$$\left.\begin{aligned} &\text{a) } A_2 = r_0 r_1 A\left[\frac{e^{-r_0 t}}{(r_2 - r_0)(r_1 - r_0)} + \frac{e^{-r_1 t}}{(r_2 - r_1)(r_0 - r_1)} + \frac{e^{-r_2 t}}{(r_0 - r_2)(r_1 - r_2)}\right] = \\ &= n(n-1)A_0\left[\frac{e^{-r_0 t}}{(n-2-n)(n-1-n)} + \frac{e^{-r_1 t}}{(n-2-n+1)(n-n+1)} + \right. \\ &\left. + \frac{e^{-r_2 t}}{(n-n+2)(n-1-n+2)}\right]; \\ &\text{b) } A_2 = n(n-1)A_0\left[\frac{e^{-nk_1 t}}{2} - e^{-(n-1)k_1 t} + \frac{e^{-(n-2)k_1 t}}{2}\right], \end{aligned}\right\} \tag{35}$$

where k_1 is r for one atom in a molecule AX_n. Similarly

$$A_i = n(n-1)\ldots(n-i+1)A\left[\frac{e^{-nk_1 t}}{\Pi_1} + \frac{e^{-(n-1)k_1 t}}{\Pi_2} + \cdots + \frac{e^{-(n-i)k_1 t}}{\Pi_i}\right], \tag{36}$$

where Π_i are geometrical series of the type $|i!|$.

Both Π_i and the consecutive terms in the square parentheses of Eq. (36) are series with alternating signs.

Finally, we derive the equation for the last, nth member of the substitution series. Since the molecules AX_n are not changed further in the defined conditions,

$$\frac{dA_n}{dt} = r_{n-1}A_{n-1}, \tag{37}$$

by replacing A_{n-1} by the expression for it from Eq. (36), we have

$$\frac{dA_n}{dt} = n!\,Ak\left[\frac{e^{-nk_1 t}}{\Pi_1} + \cdots + \frac{e^{-k_1 t}}{\Pi_{n-1}}\right]. \tag{37a}$$

Equations (33a), (36), and (37a) are too complex for clarity. We shall therefore apply them to the simplest case of isotopic substitution of AX_3 molecules by the mechanism under consideration, and for simplicity we shall take A as equal to unity. If A = 1, the concentration of AX_3 molecules will fall strictly exponentially according to the equation

$$A_0 = e^{-3k_1 t}. \tag{38}$$

This is represented by Curve 1 in Fig. 78. For concentration A_1 the following equation is valid:

$$A_1 = 3e^{-r_1 t} - 3e^{-r_0 t} = 3e^{-2k_1 t} - 3e^{-3k_1 t}. \tag{38a}$$

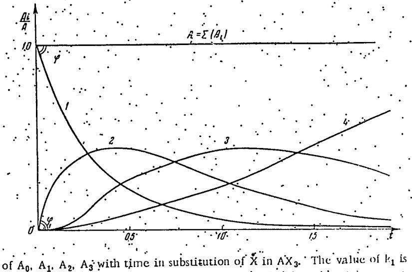


Fig. 78: Variations of A_0, A_1, A_2, A_3 with time in substitution of $\overset{*}{X}$ in AX_3. The value of k_1 is taken as 1. The abscissa axis represents a dimensionless quantity – the fraction of molecules with a given content of $\overset{*}{X}$ atoms from 0 (A_0) to 3; 1) A_0/A, 2) A_1/A, 3) A_2/A, 4) A_3/A.

At the start of the reaction the decrease of A_0 is equal to the increase of A_1

$$\Delta A_0 = \Delta A_1. \tag{39}$$

The initial regions of A_0 (t) and A_1(t) are linear, and the angles formed by them with the straight line ΣA_i A and the abscissa axis (φ and φ_1) in Fig. 78 are equal. However, subsequently, the growth of A_1 lags behind the decrease of A_0 because A_1 is consumed in formation of A_2. It is easy to show that the curve A_1(t) passes through a maximum, the position of which is easily found by equating the first derivative to zero. This gives

$$t_{\max}(A_1) = \frac{\ln(3/2)}{k_1} = \frac{3\ln(3/2)}{r_0} = \frac{2\ln(3/2)}{r_1} \tag{40}$$

when $k_1 = 1$, $t_{\max} = 0.405$.

Substitution into Eq. (38a) gives the value of A_{1max}:

$$A_{1\,max} = 3e^{-2\ln 3/2} - 3e^{-3\ln 3/2} \quad \text{or}$$

$$A_{1\,max} = 3\left[\left(\frac{2}{3}\right)^2 - \left(\frac{2}{3}\right)^3\right] = 4/9 = 0.444. \qquad (41)$$

When $A \neq 1$ $A_{1max} = 0.444A$.

We now perform similar calculations for A_2. On the assumption that A = 1 we have from Eq. (35)

$$A_2 = 3 \cdot 2\left[\frac{e^{-r_0 t}}{2} - e^{-r_1 t} + \frac{e^{r_2 t}}{2}\right],$$

and $A_{2\,max}$ can be found from the expression

$$A_{2\,extr} = 3e^{-3k_1 t}{}_{extr} - 4e^{-2k_1 t}{}_{extr} + e^{-kt}{}_{extr} = 0$$

or

$$4e^{-k_1 t}{}_{extr} - 3e^{-2k_1 t}{}_{extr} = 1.$$

Putting $e^{-k_1 t}{}_{extr} = x$, we solve the quadratic equation

$$x^2 - \frac{4}{3}x + \frac{1}{3} = 0.$$

The roots of this equation $x_1 = e^{-k_1 t'}{}_{min} = 1$, $t'_{min} = 0$ correspond to the minimum at the coordinate origin, $x_2 = e^{-k_1 t''}{}_{max} = 1/3$, $-k_1 t''_{max} = -\ln 3$ corresponds to the maximum or

$$t_{max}(A_2) = \frac{\ln 3}{k_1} = \frac{1.099}{k_1}; \qquad (42)$$
$$t_{max}(A_2) : t_{max}(A_1) \approx 2.5.$$

This $t_{max}(A_2)$ corresponds to

$$A_{2max} \approx 6\left[\frac{1}{2e^3} - \frac{1}{e^2} + \frac{1}{2e}\right] \approx 0.440.$$

From these expressions and Fig. 78, the following general result may be formulated:

The times required to reached maximum A_i increase with i more rapidly than i does;* at the same time the maxima become more flat, but, in the first approximation, their heights do not change. Therefore the average time required for formation of A_n

$$t_{n^1/_2} > nt_{0^1/_2}. \qquad (43)$$

The greater the value of n, the greater the decrease of r in passing to the last stage, and the more pronounced this inequality becomes. Except at the start, when A_0 predominates; and the very end, with A_n predominant; no single A_i predominates sharply at any instant. For most of the time two or three compounds A_i have similar values of the order of a few tenths. This is easily illustrated graphically by a plot of $\Omega_i = \frac{A_i}{A}$ for various instants of time. The formation of two sharp peaks at i = 0 and i = n, or i = 0 and i = n−1 is impossible with this mechanism.

The sequence in the appearance of molecules of different degrees of substitution is entirely different in exchange involving active intermediate forms, shown in Fig. 77. In this case molecules of maximum or nearly maximum substitution appear at once (see Chapter III), and when $[B] \gg [A_0]$ these forms predominate during the whole time of the exchange, from the lowest values of t. We shall not consider the more complex exchange which involves nothing new in principle, when [B] is of the same order as [A] and when [B] < [A].

Let us examine in greater detail exchange involving labile forms which exchange completely. Suppose that, as in the previous instance, [B] is very large, $[B] \gg [A]$, and $\rho_{B_0} = 1$, i. e., when t = 0 BX consists entirely of tagged molecules. Suppose further that only the molecules Y, which constitute a definite fraction of the AX_n molecules, actually exchange. At first we shall not consider the mutual conversions of Y and AX_n. We denote by ${}_{0.5}\overline{\tau}_1$ the average time required for the exchange of one atom in half the AX_n molecules. It is known that ${}_{0.5}\overline{\tau}_i = \frac{1}{r_i}$.

In each succeeding step τ_i will be larger because of the decrease of r caused by a decrease of the number of unsubstituted atoms in the molecule. It is easy to see that

$$\overline{\tau}_i = \frac{1}{k_1}\left(\frac{1}{n} + \frac{1}{n-1} + \ldots + \frac{1}{n-i+1}\right),$$
$$\overline{\tau}_n = \frac{1}{k_1}\left(\frac{1}{n} + \frac{1}{n-1} + \ldots + 1\right).$$

This gives the following numerical series of $\overline{\tau}$ for AX_4 molecules:

$${}_{0.5}\overline{\tau}_1 = 0.25 \cdot k_1^{-1}$$
$${}_{0.5}\overline{\tau}_2 - {}_{0.5}\overline{\tau}_1 = 0.33\, k_1^{-1}$$
$${}_{0.5}\overline{\tau}_2 = 0.58\, k_1^{-1}$$
$${}_{0.5}\overline{\tau}_3 - {}_{0.5}\overline{\tau}_2 = 0.55\, k_1^{-1}$$
$${}_{0.5}\overline{\tau}_3 = 1.08\, k_1^{-1}$$
$${}_{0.5}\overline{\tau}_4 - {}_{0.5}\overline{\tau}_3 = 1.0\, k_1^{-1}$$
$${}_{0.5}\overline{\tau}_4 = 2.08\, k_1^{-1}$$

${}_{0.5}\tau_n$ slowly increases with increasing n. When n = 10 its value is still only $3.1 k_1^{-1}$. We may conditionally take $3\,{}_{0.5}\tau_n$ to be the time for the full conversion of ${}_{\infty}\tau_n$ molecules of Y, present in the original system, into $A\overset{*}{X}_n$ molecules. When n = 4 this will be $\sim 6k_1^{-1} = 24\,{}_{0.5}\overline{\tau}_1$, and when n = 10 it will reach $93\,{}_{0.5}\tau_1$. In time $\sim {}_{\infty}\tau_n$ all the changes of concentration of the individual substitution products, shown in Fig. 78, will be completed and at any $t > {}_{\infty}\tau_n$ the distribution of products of different degrees of substitution will be represented by a curve with two peaks (Fig. 79). One of these, at i = 0 has height Ω not differing greatly from A_0, and the other, lower, has $\Omega \ll A_0$ at i = n. All intermediate forms, including substituted molecules with i = 1 and i = 2, are practically absent. If conversion of A into Y with $t_{1/2} \gg n\tau_1$ is taken into account, this results in a change in the content of unsubstituted molecules $AX_n(A_0)$ and completely substituted $A\overset{*}{X}_n(\overset{*}{A}_n)$ with time according to an exponential law, as shown in Fig. 80, a and b.

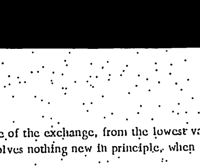


Fig. 79. Distribution of molecules of different degrees of substitution for a certain particular value of t; $t_{1/2} > t \gg s \cdot \overline{\tau}_1$.

$$A_0 = Ae^{-\tau_{1/2}^{-1} t},$$
$$\overset{*}{A}_n = A(1 - e^{-\tau_{1/2}^{-1} t}). \qquad (44)$$

---

* As in original – Translator.

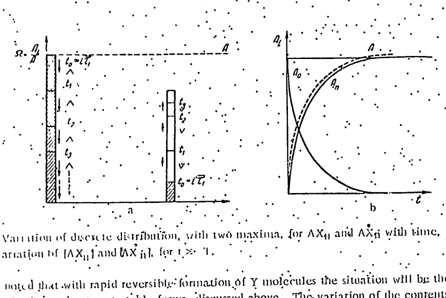


Fig. 80. a) Variation of discrete distribution, with two maxima, for AX_n and $A\overset{*}{X}_n$ with time, for t ≫ T; b) kinetics of the variation of $[AX_n]$ and $[A\overset{*}{X}_n]$, for t ≫ T.

It should be noted that with rapid reversible formation of Y molecules the situation will be the same as in consecutive substitution without metastable forms, discussed above. The variation of the contents of molecules of different degrees of substitution with time will be essentially different if B is of the same order of magnitude as A. In this case B decreases as molecules AX_n substituted with $\overset{*}{X}$ accumulate, and therefore at limiting true equilibrium, depending on the ratio B/A, we shall have some distribution Ω_i with a maximum at some definite value of $i < n$, for example, at $i = 3$ or $i = 6$. If B is sufficiently low, molecules not containing $\overset{*}{X}$ may be the most probable. For the final result, not the ratio B/A but the ratio $\overset{*}{X}/X$ in the system, i. e. $\rho_{\overset{*}{B}_0} \cdot B/nA$ is important.

The final equilibrium cannot depend on the mechanism by which it is established. However, the intermediate stages through which the system passes in the two cases under consideration are different. In consecutive transitions from mono- to di-, and then tri- and polysubstituted molecules, the equilibrium will influence the isotopic composition the whole time, and instead of the situation represented in Fig. 78, a different picture, shown in Fig. 81, will be obtained. The only similarity between Fig. 81 and Fig. 78 is the existence of maxima for all $\overset{*}{A}_i$ at $t = i\tau_1 = \frac{i}{k}$. However, with a limited supply of $\overset{*}{X}$ in the donor, after the maximum is reached the decrease continues only to values corresponding to true equilibrium, different for different i. Each consecutive maximum is lower than the one before. The intersection of the tails of the curves, shown in Fig. 81, is characteristic.

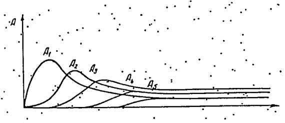


Fig. 81. Variation of $\overset{*}{A}_i$ with time with $A\overset{*}{X}_3X_{n-3}$ molecules predominant at equilibrium.

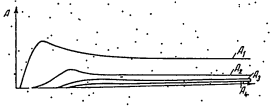


Fig. 82. Variation of $\overset{*}{A}_i$ with time with $A\overset{*}{X}X_{n-1}$ molecules predominant at equilibrium.

The distribution of isotopic molecules of different degrees of substitution varies with time in a different manner if the exchange takes place through a labile, slowly forming product. In this case, when $\rho_{B_0} = 1$, the distribution will first be of the form shown in Figs. 79 and 80a for t ≈ 0. Depending on the ratio $[\overset{*}{X}]/[X]$, for a period of time $\rho_{\overset{*}{X}_i}$ will increase and $\rho_{\overset{*}{X}_0}$ will decrease without formation of molecules of intermediate degrees of substitution, the limited supply of the total number of $\overset{*}{X}$ atoms will then begin to take effect. This will produce a decrease of $\rho_{\overset{*}{X}_s}$ with a simultaneous increase of ρ for all intermediate degrees of substitution. Depending on the value of the ratio $\overset{*}{X}/X$, ultimately the system will reach an equilibrium state with a maximum specific content of $\overset{*}{X}$ in molecules with a definite number i of $\overset{*}{X}$ atoms. At $i_{\max\ equil} = 0$ in this new distribution all the values of ρ_{X_n} decrease with increase of i. At $i_{\max\ equil} > 0$ there is a maximum at a certain value of i, while all the $\rho_{X_i} : \rho_{X_{i-1}}$ ratios should vary as shown in Fig. 82. The fairly complex and not very explanatory equations for the variations of individual values of $\rho_{\overset{*}{X}_i}$ with time are not given here.

The foregoing applies to exchange with a concentrated tagged isotope donor. All the effects described above disappear in exchange with a donor with a low content of $\overset{*}{X}$. At B ≫ A, and at B ≈ A and B ≪ A, with either exchange mechanism, practically no disubstituted or more highly substituted products will be formed, and molecules of $A\overset{*}{X}X_{(n-1)}$ will be produced in an amount increasing with time according to an exponential law. The contents of di- and higher substituted molecules $A\overset{*}{X}_2X_{n-2}$, etc., will vary with time, differently for the two mechanisms. However, this will have practically no influence on the exchange kinetics because of the small fraction of $\overset{*}{X}$ present in $A\overset{*}{X}_iX_{n-i}$ molecules, which corresponds to molecules with i > 1. For the same reason, changes in the proportions of $\overset{*}{X}$ found in forms with different i are difficult to detect and are generally not large. For many isotopic elements, even at the present time, preparations with high contents of ordinary isotopes are predominantly or exclusively in use. This is especially typical for artificial radioactive isotopes, the preparation of which without the use of carriers cannot always be effected. On the other hand, only a few elements tend to form compounds containing several or many atoms in the molecule. These two circumstances restrict the occurrence of the effects under consideration. They are primarily typical for hydrogen and the halogens, in principle they are possible also for oxygen, nitrogen, sulfur, carbon, and silicon, although in these latter elements true isotopic exchange between atoms is relatively rare. The same questions arise, however, in the exchange of stable groups or molecules with a tendency to pass from one form into another without destruction or considerable changes of structure. Such groups include cyanide ions, and water and ammonia molecules in complex compounds

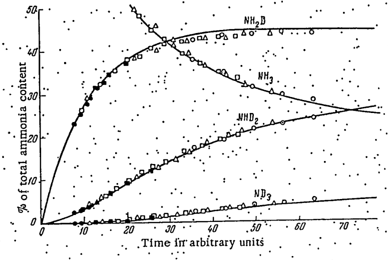


Fig. 83. Relative amounts of deuteroammonia formed from an equimolar mixture of ammonia and deuterium – theoretical amounts found by integration of equations, after Kemball [38]: △) 8.9 mg nickel at 115.3°C, 1 division = .485 minutes; ⊙) 3.2 mg platinum at −24.1°C, 1 division = 0.290 minutes; □) 6.9 mg tungsten at 143.0°C, 1 division = 0.700 minutes; ●) 2.9 mg silver at 298°C, 1 division = 2.90 minutes, ■) 6.6 mg copper at 245°C, 1 division = 1.89 minutes.

Fairly extensive experimental material is now available on the sequence of hydrogen substitution in various compounds containing several hydrogen atoms in the molecule. The investigations have been performed in homogeneous solutions of hydrocarbons with deuterosulfuric acid, and with hydrocarbons and ammonia with hydrogen and water in presence of metallic and oxide catalysts (see also Chapter III). Both the types of exchange discussed above were observed, in addition to more complex cases not provided for by the scheme.

A typical example of consecutive formation of molecules with different degrees of substitution is provided by the exchange of ammonia with deuterium, studied by Kemball [38] in presence of various metal films (Pt, Rh, Pd, Ni, Fe, Cu, Ag). The primary product in all cases was monodeuteroammonia NH_2D, from which molecules with two and three deuterium atoms were consecutively formed. The course of the process is shown in

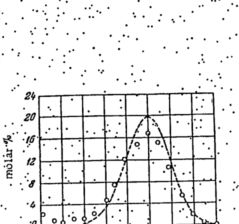


Fig. 84. Exchange of 2-methylhexane with a deuterated catalyst, comparison of observed distribution and the values calculated on the assumption of a statistical distribution [39]. O) Observed values, ---) calculated values.

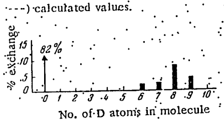


Fig. 85. Exchange of isobutane with deuterated aluminosilicate catalyst [41].

Fig. 83. By a suitable selection of the time scale, the results of experiments performed with different metals under different conditions are plotted on the same theoretical curves calculated from the experimental data and equations similar to those derived above. It was assumed in the derivation that the rate constants k_1 per atom in consecutive substitutions are equal, and that there were no kinetic isotope effects. In the same way, according to Hindin, Mills, and Oblad [39], hydrogen of paraffinic hydrocarbons containing tertiary carbon atoms can exchange under suitable conditions with hydrogen introduced into aluminosilicate catalysts in the form of heavy water. This is illustrated in Fig. 84, which refers to exchange of 2-methylhexane with a deuterated catalyst.

At the same time, sharply nonequilibrium distributions of the products have been repeatedly observed in homogeneous and heterogeneous exchange of hydrogen in hydrocarbons with deuterium, deuterosulfuric acid, and deuterated water. For example, Kemball [40], in the exchange of CH_4 with D_2 on nickel, observed direct formation of CD_4 without previous formation of methane with other numbers of deuterium atoms in any appreciable concentrations. Hindin, Mills, and Oblad [41], in an investigation published in 1951 on the exchange of isobutane with deuterated aluminosilicate catalyst, obtained, under certain conditions, products with a super-equilibrium concentration of polydeuterated molecules. This is illustrated in Fig. 85. Similar observations are reported by Otvos, Stevenson, Wagner, and Beeck [42] for the isotopic exchange of isobutane and other alkanes of iso-structure with deuterosulfuric acid. All these results are in qualitative agreement with the views detailed above. Unfortunately, quantitative comparisons with our equations are difficult owing to the lack of detailed kinetic data in these publications.

British investigators have also found even more complex relationships in systematic studies of exchange in presence of catalysts. For example, the products obtained in presence of some metals contain some very peculiar distributions of molecules by their deuterium content, which do not fit into any of the limiting cases. Figure 86 gives data on the exchange of propane, isobutane, and neopentane with D_2 over rhodium. One explanation of such results can be the assumption of an inhomogeneous catalyst surface, which includes, in addition to regions at which the exchange proceeds to completion through active radicals, also regions at which slow stepwise exchange occurs. If these two types of exchange are completely independent of each other, curves with peaks for one and n atoms of D may be obtained. Thus, widely heterogeneous surfaces may result in any form of curves for the distribution of D in the products. Such a mechanism is possible only in heterogeneous exchange. It is possible to attempt to explain such results by the presence of groups with sharply different rates for the elementary exchange step in the molecules. With this mechanism, quite natural for complex molecules, kinetic substitution maxima may appear for any number of D atoms in the molecule, other than 1 and n or n - 1. Anderson and Kemball [43] advanced a more special explanation of the maxima at intermediate values of i, based on the characteristics of the geometrical position of the hydrocarbon molecule on the surface, in accordance with A. A. Balandin's multiplet concepts. This mechanism is examined in greater detail in § 7, Chapter VI. In this connection mention should also be made of the work of Bond and Turkevich [44], who studied the catalytic exchange of trimethylene (cyclopropane) complicated by a chemical reaction. They consider the superposition of two exchange mechanisms, involving propyl in one case, and the trimethylene radical in the other, as proved. Further development of this research trend should yield important results both for the theory of isotopic exchange, and for the theory of catalysis.

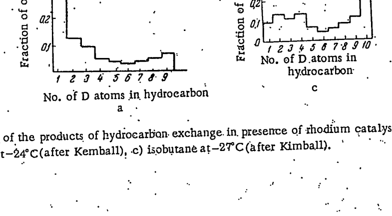


Fig. 86. Distribution of the products of hydrocarbon exchange in presence of rhodium catalyst. a) Neopentane at 99°C, b) propane at −24°C (after Kemball), c) isobutane at −27°C (after Kimball).

As was noted earlier, in the kinetic sense isotopic exchange is of the same character in the presence of several chemical forms of the element in one of the exchanging compounds, and in the exchange of a donor with a mixture of several substances of the type A_iX. The situation is more complex in isotopic exchange which proceeds by way of long-lived labile forms. In this case there are no complete analogs of the multiple substitution type discussed above. Both complications are met in isotopic exchange accompanying chemical reactions, as the reacting systems are often very complex mixtures of molecules, most of which contain several or many atoms of hydrogen and carbon, and often of other elements. Characteristic examples are the alcohol–hydrocarbon mixtures formed in the "synthol" process, and the products of pyrolysis and cracking of heavy petroleum fractions. In such systems the total number of parallel types of isotopic exchange reactions is very large, and there is no practical sense in the derivation of general equations by simultaneous solutions of all the possible particular equations for the exchange kinetics of separate substances and bond types. In such cases statistical methods are more suitable.

In Chapter III attention was drawn to the frequent occurrence of isotopic exchange which consists of the transfer of stable groups, acid anions, and neutral inorganic and organic molecules within the inner structure of crystal hydrates. In cases in which a charged or neutral group [CN^-, NH_3, CO_3^{2-}, $C_2H_4(NH_2)_2$, etc.] is exchanged as a whole with similar groups or molecules of different isotopic composition, the same laws should apply to the kinetics of the integral exchange and the formation of species of different degrees of isotopic substitution, as to the isotopic exchange of individual atoms and atomic ions; a new feature is the simultaneous transfer of isotopes of two or more elements contained in the transferred group, such as C and N in cyanide, C, N, and S in thiocyanate, H and O in water, etc.

In hydrates, cyanides, and ammines the joint transfer of isotopes of two or more elements is evident from the general chemical properties of the exchanging substances but, despite this, verification of the quantitative equality of the isotopic exchange rates of all the elements contained in a group is of great interest as it reveals new possibilities for the detection and study of such processes in the groups. For example, it is possible in this way to investigate the mobility of hydrogen in water in a crystal hydrate and in solution from the difference of the exchange rates of H and O accompanying the exchange of water. Subsidiary chemical reactions can be detected in this way, etc. Examples are provided by the study made by A. I. Brodsky et al. [45] of the structure of polythionates, and Ya. Fialkov and Yu. P. Nazarenko's investigation [46] of solutions of green chromium sulfate with the isotopic exchange of radioactive sulfur.

We shall examine in rather greater detail the first of these investigations, in which isotope methods were used to prove the validity of D. I. Mendeleev's view [47] that polythionic acids are derivatives of hydrogen di- and polysulfides H_2S_2 and H_2S_n, in which two hydrogen atoms are replaced by two (SO_3H) groups. By using tagged sulfur compounds for the synthesis of polythionic acids and studying their chemical reactions A. I. Brodsky and R. K. Eremenko [48] showed, in agreement with the results of Christiansen and Drost-Gansen [49], Aten [50], and

Lava [51], that whole sulfate and thiosulfate groups are transferred in these reactions, and distinctions between sulfide and oxidized sulfur are retained. A detailed comparison of his own data with literature data enabled A. I. Brodsky [15] to show very convincingly that the conclusions which follow from D. I. Mendeleev's theory are confirmed in every detail.

With the extension of the range of elements for which isotopes suitable for use as tagged atoms are known, the question of the simultaneous isotopic exchange of two or more elements has become of independent importance.

It is quite possible to tag hydrogen and carbon; or hydrogen, halogen, and oxygen, etc., simultaneously, in a molecule. Up to a point this occurs spontaneously because a number of the elements of the greatest interest in kinetics have two or more isotopes in the normal native state. In this connection we may mention the obligatory presence of protium and deuterium in hydrogen, of O^{16}, O^{17}, and O^{18} in oxygen, of C^{12}, C^{13}, and usually C^{14} in carbon, Cl^{35} and Cl^{37} in chlorine, etc.

The behavior of a system during simultaneous exchange of two or more elements depends on the chemical structure of the exchanging elements and on the mechanism of the exchange. If the exchange of each of the elements occurs with transfer of atoms or atomic ions, we may expect more or less completely independent exchanges of the different elements. For example, we may readily imagine exchange between alkyl halides and aryl halides in which the exchange rates of hydrogen and of halogens are entirely different. In the isotopic exchange of complex metallic compounds the exchange of the central metal ions typically proceeds by an electronic mechanism, while the atoms in the outer shell of the complex are exchanged by activation, association, or dissociation mechanisms. In particular, in the exchange of $[Fe(CN)_6]^{4-}$ with $[Fe(\overset{*}{C}N)_6]^{3-}$ with molecules tagged in Fe and cyanide nitrogen, it is natural to expect rapid exchange of the central cation by charge transfer and very slow exchange of CN ions. If the Fe^{2+} has outer shells of 6 tagged $C\overset{*}{N}$ ions, and the Fe^{3+} has 6 untagged CN ions, the exchange should result in the formation of exactly the same numbers of complexes with Fe^{3+} and all six cyanide groups tagged simultaneously, while complexes with mixed shells, such as

$$[\overset{*}{Fe}{}^{2+}(C\overset{*}{N})_5(CN)]^{4-}, \quad [\overset{*}{Fe}{}^{3+}(C\overset{*}{N})_2(CN)_4]^{3-},$$

would not appear for a long time. In the other extreme case of exchange by means of whole groups, the rates and the influence of the kinetic factors should be the same for the isotopic exchange of all the elements present in the group. This is typical for C and N, C and O, etc. From this it is clear that a quantitative comparison of the isotopic exchange kinetics for two or more elements contained in a molecule can provide valuable information on the exchange mechanism. This method also seems likely to prove very effective for investigation of the mechanisms of elementary chemical reactions.

§ 7. Statistical Theory of Exchange in a System with a Large Number of Acceptors

Kinetic analysis of systems containing numerous species with different rate constants was first carried out in theoretical studies of adsorption and catalysis at heterogeneous surfaces.

In many cases the kinetics of adsorptional and catalytic processes does not conform to the equations theoretically derived for analogous processes at homogeneous surfaces in the absence of distortions caused by interactions of the adsorbed molecules. A general theory of such processes, in good agreement with experimental data, has been developed on the basis of the statistical theory. The conclusions and concepts of this theory can be easily applied to isotopic exchange in presence of a large number of qualitatively distinct acceptors.

We first consider exchange in a system consisting of a donor of isotope $\overset{*}{X}$, present in the form of gaseous or dissolved molecules $B\overset{*}{X}$, and molecules of the type $AX_{i_1}^{\alpha}X_{i_2}^{\beta}X_{i_3}^{\gamma}X_{i_4}^{\delta}$, etc., in which α, β, etc. represent different structural positions of X atoms in the molecule. The kinetic properties of the system may be represented graphically by showing the contents of the different types of atoms by columns in a diagram in which each column refers to a definite isotopic exchange rate constant. This gives a diagram of the type shown in Fig. 87. It gives the statistical characteristics of the isotopic exchange rate constants. This is an example of a discrete distribution $\Omega(k)$ by values of k. It may be approximately replaced by a continuous line. The more bond types there are in a molecule, and the closer together the corresponding values of k, the closer will be the columns in the diagram, and the better will the smooth curve represent the discrete distribution. The function $\Omega(k)$ is termed the distribution function.* For continuous distributions and for discrete distributions with large numbers of closely adjacent peaks

$$\Omega(k) = \frac{dN}{dk}, \qquad (15)$$

or, in our diagram

$$\Omega(k) = \frac{dN}{d(\log k)} \qquad (15a)$$

where N is the total number of X atoms of all types in the system, apart from those contained in the BX molecules. $\Omega(k)$ will then be the number of X atoms exchanging with a rate constant k_i [or $\Omega(\log k)$ is the number of atoms exchanging with $\log k_i$]. It must be emphasized that, as Fig. 87 shows, the sequence of the peaks in the diagram does not in general coincide with the sequence in which they are given in the chemical formula. As was pointed out earlier, the values of i_1, i_2, i_3 etc. in the molecule for different positions of a particular element, for example H, vary in not very wide limits; therefore the height of the function $\Omega(k)$ changes relatively little with increase of k: $\Omega(k)$ and $\Omega(\log k)$ are close to uniformly inhomogeneous distribution (Fig. 88). The situation is different in the exchange of a common donor $B\overset{*}{X}$ with a mixture of acceptor molecules A_1X, A_2X, A_3X ... etc., as the values of their concentrations, $[A_1X]$, $[A_2X]$, etc., can vary in any desired limits. This applies also to the numbers of atoms of X n_{X_1}, n_{X_2}, n_{X_3}, etc., present in the system in different molecules.

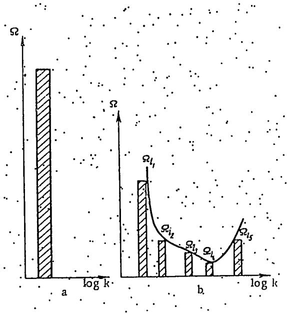


Fig. 87. a) Distribution by isotopic exchange rate constants for molecules with one type of H atoms present, in a statistical diagram on a logarithmic scale; b) discrete distribution by isotopic exchange rate constants for hydrogen in a compound YH_{17}, on a logarithmic scale. Y represents the molecule less all its hydrogen atoms. The numbers of hydrogen atoms in the five groups are $i_1 = 8$, $i_2 = 3$, $i_3 = 2$, $i_4 = 1$, $i_5 = 3$.

For complex systems, consisting of mixtures of large numbers of molecules, of which all or some are in different structural positions, the total number of bond forms of X atoms greatly increases, and the range of values of k increases also. In this case $\Omega(k)$ should be taken as the number of molecules of a particular type (in the system as a whole or in 1 cc of the system) multiplied by the number of atoms present in the given position in the system.

In such cases we may expect to find practically continuous distributions, or distributions consisting of several continuous regions separated by breaks (see Fig. 88a and b).

We shall consider only the case in which ρ_B is practically constant during isotopic exchange

$$\left.\begin{aligned} \rho_B &= \text{const}, \\ [B\overset{*}{X}] &= \text{const}. \end{aligned}\right\} \qquad (16)$$

This is the case when $[B] \gg [A]\,\Sigma\,(i_1 + i_2 + i_3 + \ldots)$ and when loss of $[B\overset{*}{X}]$ is continuously replaced.

---

* In most of our previous publications we represented the distribution function by $\rho(k)$, but this would be inconvenient here, as ρ has already been used to represent the specific isotopic contents.

In this case the process is practically irreversible and, despite the theoretical reversibility of isotopic exchange, the X atoms of each type react independently of each other.

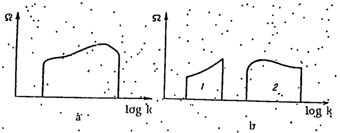


Fig. 88. Various types of distribution by log k. a) Close to uniformly heterogeneous; b) distribution with two continuous regions separated by a break.

For ideal isotopic exchange of X atoms of all types the heat effects are zero and the equilibrium constants are unity.

$$\left.\begin{array}{l} Q_1 = Q_2 = \ldots = Q_i = \ldots = 0, \\ K_1 = K_2 = \ldots = K_i = \ldots = 1. \end{array}\right\} \qquad (47)$$

Therefore we must consider the differences between different types of X only by the exchange rates and distribution, and not by the limits reached at equilibrium. This limit is also practically independent of the temperature. With our assumptions, after a sufficiently long time $\underline{t}$, for all the types of X atoms

$$\rho_{1_\infty} = \rho_{2_\infty} = \ldots = \rho_{i_\infty} = \rho_{B_0} = \rho_B. \qquad (48)$$

We shall characterize the exchange by the functions F_1, F_2, etc., and r_1, r_2, etc., respectively (see §6, Chapter II).

From Eq. (33b) in Chapter II $r_i = R_i \dfrac{[X_i] + [B]}{[X_i][B]}$, where R_i is the total rate of exchange of X atoms between BX and X atoms in the ith form. In given experimental conditions R_i can often be represented by the product of the true exchange rate constant $\underline{k}$ and a constant factor $\underline{j}$, which represents the true order of the process

$$R_i = k_i f\,\{[A_i];\,[B]\} = R_{i_\infty} e^{-E_i/RT}. \qquad (49)$$

Therefore

$$r_i = r_{i_\infty} e^{-E_i/RT} \text{ and } k_i = k_{i_\infty} e^{-E_i/RT}, \qquad (50)$$

where R_{i_∞} and r_{i_∞} include, as factors,

$$k_{i_\infty} \text{ and } f\,\{[A_i];\,[B]\}.$$

From Eqs. (34) and (37) of Chapter II, at any given instant

$$\rho_{i_\infty} - \rho_{it} = e^{-r_i t} = 1 - F_{it} = \gamma_{it}, \qquad (51)$$

in other words, the difference between the specific content of $\overset{*}{X}$ at equilibrium, ρ_{i_∞}, and the specific content of this isotope at a given instant in X atoms of the ith type (ρ_{it}) decreases exponentially with time. In the initial conditions postulated, $\rho_{i_\infty} - \rho_{it}$ is equal to $(1 - F_i)$, i. e., the fraction of $\underline{i}$ atoms which remain unexchanged at time $\underline{t}$. For brevity, we denote $\rho_{i_\infty} - \rho_{it} = 1 - F_{it}$ by γ_{it} from Eqs. (50) and (51)

$$\gamma_{it} = \exp\,[-r_{i_\infty} t e^{-E_i/RT}]. \qquad (52)$$

Let us consider that case when all r_{i_∞} are equal and the differences in the isotopic exchange rates are determined only by different values of the activation energy E_i of isotopic exchange, while the latter vary in wide limits. This case is mathematically identical with our detailed analysis [53] of irreversible chemisorption at surfaces with a wide range of E of activated adsorption. In both cases the range of distribution is determined not by the absolute difference between the extreme values of E_i, i. e., not by

$$\Delta E_i = E_{i\max} - E_{i\min} \qquad (53)$$

but by the ratio of this value to RT. A wide distribution, to which all the deductions given below are fully applicable, is the distribution which conforms to the following inequality

$$\frac{\Delta E}{RT} = \frac{E_{i\max} - E_{i\min}}{RT} \geq 4. \qquad (54)$$

It is evident that at sufficiently low temperatures all distributions become wide, and at sufficiently high temperatures, narrow.

We now compare the behavior of groups with different E_i at T = const and t = const. The variation of $\underline{r}$ with E is represented by the exponential r(E) curve shown by a broken line in Fig. 89. The same diagram shows values of γ_{it} calculated from Eq. (52) for groups with sharply different values of E at different values of $\underline{t}$. Each curve corresponds to a definite $\underline{t}$: from t_1 (top curve) to t_6 (bottom curve). These isochrones indicate, on the γ(E) graph, the consecutive positions of the boundary between exchanged and unexchanged groups. At first there is no exchange for most of the groups with large and intermediate values of E, and γ is appreciably less than 1 only for the groups with the lowest activation energies (curve t_1). Gradually new groups are progressively drawn into the exchange, until a clear boundary is formed between the exchanged groups, for which γ ≈ ≈ 0 (i. e., in which the isotopic exchange has reached equilibrium, with $\rho = \rho_B = \rho_\infty$) and groups which have not yet entered the exchange, for which γ ≈ 1. As was shown by us earlier [52, 53]; the boundary on the γ(E) graphs shifts to the right with time, remaining parallel to itself (Fig. 90b). Because of this, and as the boundary on the Ω(E) graph is steep, the intermediate region between $\gamma_i \approx 0$ and $\gamma_i \approx 1$ is narrow, and its form changes little.

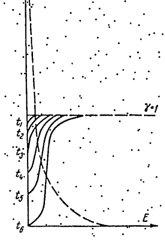


Fig. 89. Variation of $\underline{r}$ with E (broken line) and γ with E (continuous lines). Different γ(E) curves correspond to different exchange times; $t_1 < t_2 < \ldots < t_6$.

Calculation of the aggregate exchange kinetics reduces to calculation of the area occupied by the completely exchanged groups in the Ω(E) graph. For this, the true curvilinear boundary (Fig. 90c) is replaced by a vertical line through the point of inflection in the curve.

It can be easily shown that

$$E_{\text{infl}} = RT \ln t r_\infty = RT \ln \frac{t}{\tau_0}. \qquad (55)$$

We assume for simplicity that

$$\int_{E_{\min}}^{E_{\max}} \Omega(E)\,dE = 1. \qquad (56)$$

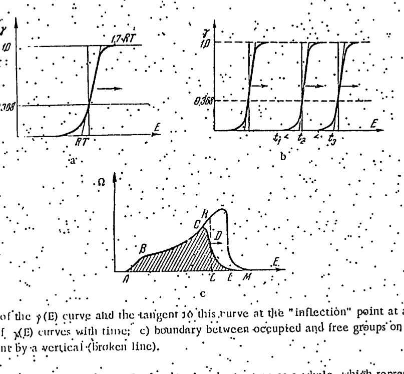


Fig. 90. a) Form of the γ(E) curve and the tangent to this curve at the "inflection" point at a certain value of t; b) displacement of γ(E) curves with time; c) boundary between occupied and free groups on the Ω(E) curve, and its replacement by a vertical (broken line).

In this formulation the relative exchange F_Σ for the complex system as a whole, which represents the fraction of the final equilibrium exchange of all the X atoms, is expressed to a good degree of approximation by the equation

$$F_\Sigma = F_\Sigma(t) = \int\limits_{E_{\min}}^{E=RT\ln\frac{t}{\tau_0}} \Omega(E)\,dE = \int\limits_{E_{\min}=RT\ln t_{\min}-c}^{E=RT\ln t-c} \Omega(E)\,dE. \qquad (57)$$

It is now possible to use the known function Ω (E) to determine the form of the kinetic isotherm for isotopic exchange. Conversely, if the form of the function $F_\Sigma(t)$ is experimentally determined in analytical or graphical form, it is easy to find the function for the distribution of the groups by activation energies

$$\Omega(E) \approx \frac{dF_\Sigma(t)}{RTd\ln t} = \frac{t}{RT}\frac{dF_\Sigma(t)}{dt}. \qquad (58)$$

By using the far-reaching similarity between the kinetics of isotopic exchange in complex systems and the kinetics of activated adsorption on complex surfaces, we may write directly, without deriving it, the expression for the kinetic isosteres t = t(T) when E_{boundary} const

$$\left.\begin{aligned} &\text{a) } t = \tau_0 e^{E/RT};\\ &\text{b) } \ln t = \ln \tau_0 + \psi \frac{1}{T}. \end{aligned}\right\} \qquad (59)$$

For all Ω (E) the logarithm of the time required to reach a definite F_Σ will increase linearly with the reciprocal of the temperature but the coefficient ψ in the T^{-1} term is differently related to F_Σ for different types of distribution, $\psi = \psi(F_\Sigma)$. In particular, for uniform distribution, when Ω(E) ≈ const (Fig. 91)

$$\psi - \frac{F_\Sigma}{HR},$$

where R is the gas constant and H is the height of the distribution. Similarly, for the isochrones $F_\Sigma = F_\Sigma(T)$ at t = const, the equation

$$F_\Sigma(T)_{t=\text{const}} = \int\limits_{E_{\min}}^{CT} \Omega(E)\,dE, \qquad (60)$$

must be valid, while to find Ω(E) from the isochrones the equation

$$\Omega(E) \approx \frac{dF_\Sigma(T)}{CdT} \qquad (61)$$

may be used, etc. By a combination of static and dynamic methods for the study of isotopic exchange it is easy to obtain isochrones for wide temperature variations and to use them to find Ω(E).

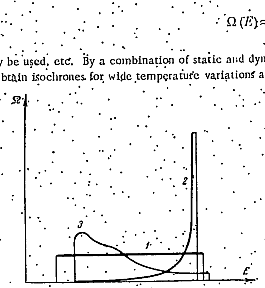


Fig. 91. Examples of types of distribution: 1) regular, 2) exponential, 3) narrowing.

For a more exact solution of the problem the mathematical equations derived by V. I. Levin [54] for adsorption kinetics can be used. Unfortunately, the increased accuracy is attained at the cost of a considerable increase of mathematical complexity. This also applies to the mathematical methods developed in the adsorption theory by O. M. Todes et al. [55] and in the theory of catalytic reactions by M. I. Temkin [56]. In principle, these methods can be applied to the kinetics of isotopic exchange.

A characteristic feature of the kinetics of systems with a wide range of E is the frequent occurrence of slowly descending logarithmic (62) and parabolic kinetic curves (63):

$$F_\Sigma = a\ln t + c; \qquad (62)$$

$$F_\Sigma = at^1/n - c. \qquad (63)$$

In Eqs. (62) and (63), with T = const, a and c are constants, and n > 1.

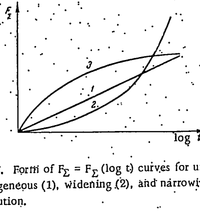


Fig. 92. Form of $F_\Sigma = F_\Sigma$ (log t) curves for uniformly heterogeneous (1), widening (2), and narrowing (3) distribution.

The nature of the distribution of groups according to E can be easily established from $F_\Sigma = F_\Sigma$(log t) graphs. A linear plot indicates that the distribution is close to uniform, a concave curve indicates widening, and a convex curve, narrowing distribution (Fig. 92).

The above theory is unreservedly applicable to heterogeneous isotopic exchange at heterogeneous surfaces, and forms the basis of quantitative kinetic isotopic methods which have played an important role in the theory of catalysis. It becomes increasingly well applicable to exchange with complex molecules and mixtures as the range of groups with different values of E for the exchanging forms becomes wider. However, as was shown in a special investigation [57], a system begins to resemble widely heterogeneous systems even in the presence of only two groups of regions with sharply different energies. Therefore the results derived for wide distributions should provide a fairly good degree of approximation for systems with several bond types, if the E/RT range is sufficiently wide. In principle, the same mathematical methods and the analogy with activated adsorption may be used to derive kinetic exchange equations for ρ_B decreasing with time. However, in this case complications arise caused by reverse exchange of the most rapidly exchanging groups, by changes of B, leading to a peculiar redistribution with BX_n acting as a peculiar catalytic carrier. This may result in maxima for individual ρ_{A_i}, and in complex kinetic isotherms. It is therefore desirable to use, if possible, constant or little changing ρ_B, while if this is impossible, the kinetic characteristics of the most reactive groups should be determined in separated experiments performed at low temperatures.

§8. Complications of Isotopic Exchange Kinetics Caused by Thermodynamic Isotope Effects

The exponential kinetic equations given in Chapter II are, strictly speaking, applicable only to ideal uncomplicated exchange which ends in equipartition of the particular isotope between the two forms present.

For light elements, and especially for hydrogen, this approximation is not always permissible, and the nature of the distortions introduced into the kinetics by the thermodynamic nonideality of the exchange is a peculiar reflection of the mechanism of the process. In recent years there have been several successful attempts to derive kinetic equations for nonideal exchange; the results of these are presented in this section.

a) Approximate equations for molecules containing several atoms of the exchanging isotope in the same chemical position

Considerable mathematical difficulties are involved in simultaneously taking into account the complications caused by participation of more than two atoms of an isotope in exchange together with thermodynamic isotopic corrections. Therefore approximations which restrict the applicability of the results are used in studies of the kinetics of nonideal isotopic exchange. One such approximation concerns the method for taking into account the participation of more than two atoms in the exchange. In exchange of $AX_{m-g}\overset{*}{X}_g$ molecules with $BX_{n-h}\overset{*}{X}_h$ molecules all the m positions of the X atoms in AX_m molecules are assumed identical, and the n positions of the X atoms in BX_n molecules are also regarded as equivalent. Further, kinetic isotope effects are not considered at all.

Moreover, the exchange is assumed to proceed by a simple association or dissociation mechanism without participation of rapidly exchanging intermediate forms which result in super-equilibrium concentrations of polysubstituted molecules. It was shown by Harris [58], and also by Bunton, Halevi, and Llewellyn [59], that with these assumptions the presence of several X atoms in the molecules is equivalent to an increase of the initial constant concentrations of the exchanging substances. On this basis we may use Eqs. (36) and (37) of Chapter II, to write the final equations for the exchange kinetics

$$-\ln(1-F) = R\frac{m[A]+n[B]}{mn[A][B]}t \tag{64}$$

or, for the case in which at the start of the experiment one of the substances, as A, contained no tagged atoms at all,

$$-\ln(1-\gamma) = R\frac{m[A]+n[B]}{mn[A][B]}t, \tag{65}$$

where $\gamma = \frac{[\overset{*}{A}]}{[\overset{*}{A}]_\infty}$ is the ratio of the instantaneous concentration of $\overset{*}{X}$ atoms in the substance AX_n to the final concentration of the same atoms established at $t = \infty$, i. e., at equilibrium. It is easily seen that

$$[\overset{*}{X}]_\infty = \frac{mn[\overset{*}{B}_0][A_0]-[\overset{*}{A}_0][B_0]}{m[A]+n[B]}. \tag{66}$$

The expression which connects R with the half-exchange time is

$$R = \frac{0.693}{t_{1/2}}\left[\frac{mn[A][B]}{m[A]+n[B]}\right]. \tag{67}$$

b) Allowance for nonideality of the exchange

Equations (64-67) do not allow for deviations of K from 1 and of the final distribution of $\overset{*}{X}$ from equipartition. When

$$K = \frac{k_1}{k_2} \neq 1 \tag{68}$$

the statement in §6, Chapter II concerning the equality of the rate constants for the forward and reverse exchange reactions is no longer true. Let us first consider Harris' examination of the corrections introduced by the inequality (68) into the kinetics of the simplest case of bimolecular exchange of AX + BX molecules, when n = m = 1. The author shows that in this case

$$-\ln(1-\gamma) + \ln\left\{1-\gamma\left(\frac{K-\sqrt{K}}{K+\sqrt{K}}\right)\right\} = \frac{2k_1[A_0]}{\sqrt{K}}t; \tag{69}$$

$$[\overset{*}{X}]_\infty = [A_0]\left(\frac{K-\sqrt{K}}{K-1}\right).$$

He also gives the following expression for the relationship between the rate constant for the forward exchange k_1 and the half-exchange time $t_{1/2}$.

$$k_1 = \frac{\sqrt{K}}{2[A_0]t_{1/2}}\ln\left(\frac{K+3\sqrt{K}}{K+\sqrt{K}}\right). \tag{70}$$

A comparison of Eq. (69) with Eq. (65) and Eq. (36) of Chapter II clearly demonstrates the nature of the deviations from exponentiality which arise when $K = k_1/k_2 \neq 1$. The dependence of k_1 on the temperature should not be strictly of the Arrhenius type, as Eq. (70) contains a logarithmic term in K and $\sqrt{K}$. For very low concentrations of tagged isotopes, typical in radiochemistry, it was possible to apply the same method to more complex cases of isotopic exchange by a molecular mechanism involving p molecules of AX and q molecules of $B\overset{*}{X}$, and also dissociative exchange according to the scheme

$$\begin{aligned} AX &\xrightarrow{k_1'} A + X; \\ A + X &\xrightarrow{k_2} AX; \\ A + \overset{*}{X} &\xrightarrow{k_3} A\overset{*}{X}; \\ A\overset{*}{X} &\xrightarrow{k_4} A + \overset{*}{X}. \end{aligned} \tag{71}$$

In both cases, in agreement with our 1941 results, because of the low-specific content of $\overset{*}{X}$ the process is practically of the first order, but the exchange rate constant becomes a function of K.

The kinetics of the $pAX + qB\overset{*}{X}$ exchange follows the equation

$$-\ln(1-\gamma) = k_1[A_0]^{p-1}[B_0]^{q-1}\{K[A_0]+[B_0]\}t, \tag{72}$$

and hence,

$$k_1 = \frac{0.693K}{t_{1/2}[A]^{p-1}[B]^{q-1}\{K[A_0]+[B_0]\}} \tag{73}$$

It is clear from Eq. (73) that in this case also k_1 is not strictly exponential.

For exchange by a dissociation mechanism, the analog of Eq. (72) is

$$-\ln(1-\gamma)=k_1'\frac{\varepsilon_1[A_0]+\varepsilon_2[B_0]}{\varepsilon_1\varepsilon_2[B_0]}t, \tag{74}$$

where

$$\varepsilon_1=k_1'/k_4 \text{ and } \varepsilon_2=k_2'/k_3. \tag{75}$$

It must be stressed that Eqs. (72-74) are valid only at negligibly low concentrations of X, when $[A]\approx[A_0]$ and $[B]=[B_0]$. The considerably more complex expressions for $\ln(1-\gamma)$ and k_1 for exchange with commensurable values of [X] and [X] are not given here.

The kinetic constants in the ratios of Eqs. (75) are taken from Eq. (71). The difference between Eqs. (74), (72), and (69) must be emphasized. The nature of the corrections in the kinetic equations is highly sensitive to the mechanism, and it is hoped that in the future this may be used in studies of exchange mechanisms. At present the determination of true values of k_1 as precisely as possible is of greater importance.

For reactions with a molecular mechanism, if isotopic corrections are neglected, the rate constant is given by the equation

$$k_1'=\frac{0.6931}{[A]^{p-1}[B]^{q-1}\{[A_0]+[B_0]\}t_{1/2}}. \tag{76}$$

Its ratio to the true rate constant k_1 of Eq. (73), which allows for corrections for $K\neq 1$, can be expressed as

$$k_1'/k_1=1-\frac{K-1}{K}\left(\frac{1}{\Delta+1}\right), \tag{76a}$$

where

$$\Delta=\frac{[A]}{[B]}. \tag{77}$$

Therefore k_1' and k_1 can be brought as close together as required by an increase of the ratio of the concentration of AX to the concentration of BX.

A more complete analysis of the same problem was recently made by Bunton, Craig, and Halevi [60], who confirmed Harris' main conclusions. Special attention was paid to evaluation of the possible deviations of the exchange from strict exponentiality. The authors showed very convincingly that with the magnitude of the isotope corrections characteristic for the equilibrium constants in the isotopic exchange of carbon, oxygen, and nitrogen, such deviations in most cases may be ignored. Hydrogen is the only element for the isotopic exchange of which this may substantially distort the kinetic picture, and this is mainly true for the exchange of its simplest compounds only. For a given value of K the corrections diminish with decreasing content of the tagged isotope. This is clearly demonstrated in Fig. 93, which gives the variation of the error, as a percentage of K, for different values of

$$\rho_{B_0}=\frac{[B_0]}{m[B]}.$$

It is evident from this figure that at $\rho_{B_0}\leqq 0.2$, up to K = 1.2, the error is less than 1.5%; at $\rho_{B_0}=0.5$ the same error is obtained at K = 1.05; and at $\rho_{B_0}=1$, at K = 1.02. A curious fact is that within any one experiment the percentage error, under the same conditions, diminishes as equilibrium is approached (Fig. 94). Both graphs represent kinetics of exchange by a molecular association mechanism. Qualitatively similar but quantitatively distinct relationships are found for a dissociation mechanism.

These investigations are the first explorations in a new direction. Their principal value lies in establishing the order of magnitude of the deviations from exponentiality, and in determining the sensitivity of the resultant corrections to the reaction mechanisms. The development of a finalized theory of the rates of complicated non-ideal isotopic exchange is a task for the future.

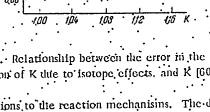


Fig. 93. Relationship between the error in the determination of K due to isotope effects, and K [60].

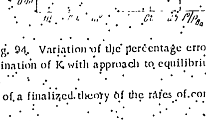


Fig. 94. Variation of the percentage error in the determination of K with approach to equilibrium [60].

§ 9. Determination of Isotopic Corrections from the Separation Kinetics

The statistical theory of kinetic isotope effects was presented in detail in the previous chapter. In cases in which it is possible to determine the differential values of the isotopic composition of the initial substances and the exchange products at definite instants of time, direct comparison between this theory and experimental data are possible. However, very often the determinations of isotopic composition are carried out after the accumulation of portions of products corresponding to a more or less considerable fraction of complete conversion. In such cases the observed values of ρ_{X_1}, ρ_{X_2}, etc., are more or less complex summated and average values for the differential composition of the reaction products, corresponding to varying isotopic composition of the initial substances and varying conversion rates of molecules of different isotopic composition. This makes it necessary to derive integral equations which relate the ratios of the kinetic constants with the separation coefficients and the degree of conversion. A considerable proportion of the actual experimental values of α and δ given in Chapter IV has been obtained with the aid of such equations. Below we give their derivation for the simplest cases, and some indication of the relationships which apply to more complex cases.

Let us consider the raction of a substance A (consisting of two isotopic forms A_1 and A_2) involving one molecule of it. The reaction may be of any type: decomposition of the molecule into parts, isomerization, combination or exchange with other molecules B or C, etc. We assume further that the chemical reaction is irreversible, and that the observed change of isotopic composition is caused entirely by this reaction, with a practical absence of isotopic exchange between the original molecules, between the molecules of the products, or between the original substances and the reaction products. With these assumptions the reaction may be regarded as two independent parallel chemical processes, connected only by the consumption of common reagents. Suppose that the molecularity of the initial reaction is represented by the equation

$$\left.\begin{aligned}A_1+B+C&=X_1+D+\\A_2+B+C&=X_2+D+\ldots\end{aligned}\right\} \tag{78}$$

This equation corresponds to the following kinetic equations for the different isotopic molecules

$$\frac{dx_1}{dt}=k_1(a_1-x_1)(b-x_1-x_2)(c-x_1-x_2), \tag{78a}$$

$$\frac{dx_2}{dt}=k_2(a_2-x_2)(b-x_1-x_2)(c-x_1-x_2). \tag{78b}$$

In these equations a_1-x_1 and x_1 represent the concentrations of A_1, X_1, etc. In this instance the ratio of the rate constants k_1/k_2 is the required kinetic isotope effect α

$$\alpha=k_1/k_2 \text{ and } \delta=\alpha-1=k_1/k_2-1. \tag{79}$$

For exchange by a dissociation mechanism, the analog of Eq. (72) is

$$-\ln(1-\gamma)=k_1'\frac{\varepsilon_1[A_0]+\varepsilon_2[B_0]}{\varepsilon_1\varepsilon_2[B_0]}t, \tag{74}$$

where

$$\varepsilon_1=k_1'/k_4 \text{ and } \varepsilon_2=k_2/k_3. \tag{75}$$

It must be stressed that Eqs. (72–74) are valid only at negligibly low concentrations of X, when $[A]\approx[A_0]$ and $[B]=[B_0]$. The considerably more complex expressions for $\ln(1-\gamma)$ and k_1 for exchange with commensurable values of [X] and [X] are not given here.

The kinetic constants in the ratios of Eqs. (75) are taken from Eq. (71). The difference between Eqs. (74), (72), and (69) must be emphasized. The nature of the corrections in the kinetic equations is highly sensitive to the mechanism, and it is hoped that in the future this may be used in studies of exchange mechanisms. At present the determination of true values of k_1 as precisely as possible is of greater importance.

For reactions with a molecular mechanism, if isotopic corrections are neglected, the rate constant is given by the equation

$$k_1'=\frac{0.6931}{[A]^{p-1}[B]^{q-1}\{[A_0]+[B_0]\}t_{1/2}}. \tag{76}$$

Its ratio to the true rate constant k_1 of Eq. (73), which allows for corrections for $K\neq 1$, can be expressed as

$$k_1'/k_1=1-\frac{K-1}{K}\left(\frac{1}{\Delta+1}\right), \tag{76a}$$

where

$$\Delta=\frac{[A]}{[B]}. \tag{77}$$

Therefore k'_1 and k_1 can be brought as close together as required by an increase of the ratio of the concentration of AX to the concentration of BX.

A more complete analysis of the same problem was recently made by Bunton, Craig, and Halevi [60], who confirmed Harris' main conclusions. Special attention was paid to evaluation of the possible deviations of the exchange from strict exponentiality. The authors showed very convincingly that with the magnitude of the isotope corrections characteristic for the equilibrium constants in the isotopic exchange of carbon, oxygen, and nitrogen, such deviations in most cases may be ignored. Hydrogen is the only element for the isotopic exchange of which this may substantially distort the kinetic picture, and this is mainly true for the exchange of its simplest compounds only. For a given value of K the corrections diminish with decreasing content of the tagged isotope. This is clearly demonstrated in Fig. 93, which gives the variation of the error, as a percentage of K, for different values of

$$\rho_{B_0}=\frac{[B_0^*]}{m[B]}$$

It is evident from this figure that at $\rho_{B_0}\leq 0.2$, up to $K=1.2$, the error is less than 1.5%; at $\rho_{B_0}=0.5$ the same error is obtained at $K=1.05$, and at $\rho_{B_0}=1$, at $K=1.02$. A curious fact is that within any one experiment the percentage error, under the same conditions, diminishes as equilibrium is approached (Fig. 94). Both graphs represent kinetics of exchange by a molecular association mechanism. Qualitatively similar but quantitatively distinct relationships are found for a dissociation mechanism.

These investigations are the first explorations in a new direction. Their principal value lies in establishing the order of magnitude of the deviations from exponentiality, and in determining the sensitivity of the resultant

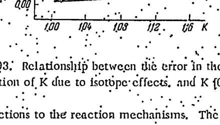


Fig. 93. Relationship between the error in the determination of K due to isotope effects, and K [60].

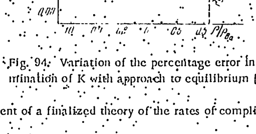


Fig. 94. Variation of the percentage error in the determination of K with approach to equilibrium [60].

corrections to the reaction mechanisms. The development of a finalized theory of the rates of complicated nonideal isotopic exchange is a task for the future.

§ 9. Determination of Isotopic Corrections from the Separation Kinetics

The statistical theory of kinetic isotope effects was presented in detail in the previous chapter. In cases in which it is possible to determine the differential values of the isotopic composition of the initial substances and the exchange products at definite instants of time, direct comparison between this theory and experimental data are possible. However, very often the determinations of isotopic composition are carried out after the accumulation of portions of products corresponding to a more or less considerable fraction of complete conversion. In such cases the observed values of ρ_{X_1}, ρ_{X_2}, etc., are more or less complex summated and average values for the differential composition of the reaction products, corresponding to varying isotopic composition of the initial substances and varying conversion rates of molecules of different isotopic composition. This makes it necessary to derive integral equations which relate the ratios of the kinetic constants with the separation coefficients and the degree of conversion. A considerable proportion of the actual experimental values of α and δ given in Chapter IV has been obtained with the aid of such equations. Below we give their derivation for the simplest cases, and some indication of the relationships which apply to more complex cases.

Let us consider the raction of a substance A (consisting of two isotopic forms A_1 and A_2) involving one molecule of it. The reaction may be of any type: decomposition of the molecule into parts, isomerization, combination or exchange with other molecules B or C; etc. We assume further that the chemical reaction is irreversible, and that the observed change of isotopic composition is caused entirely by this reaction, with a practical absence of isotopic exchange between the original molecules; between the molecules of the products, or between the original substances and the reaction products. With these assumptions the reaction may be regarded as two independent parallel chemical processes, connected only by the consumption of common reagents. Suppose that the molecularity of the initial reaction is represented by the equation

$$\left.\begin{aligned} A_1+B+C&=X_1+D+\ldots,\\ A_2+B+C&=X_2+D+\ldots \end{aligned}\right\} \tag{78}$$

This equation corresponds to the following kinetic equations for the different isotopic molecules

$$\left.\begin{aligned} \frac{dx_1}{dt}&=k_1(a_1-x_1)(b-x_1-x_2)(c-x_1-x_2), & \text{(78a)}\\ \frac{dx_2}{dt}&=k_2(a_2-x_2)(b-x_1-x_2)(c-x_1-x_2). & \text{(78b)} \end{aligned}\right\}$$

In these equations a_1-x_1 and x_1 represent the concentrations of A_1 X_1 etc. In this instance the ratio of the rate constants k_1/k_2 is the required kinetic isotope effect α

$$\alpha=k_1/k_2 \text{ and } \delta=\alpha-1=k_1/k_2-1; \tag{79}$$

Division of (78a) by (78b) gives

$$\frac{dx_1}{dx_2} = \frac{k_1}{k_2} \cdot \frac{(a_1 - x_1)(b - x_1 - x_2)(c - x_1 - x_2)}{(a_2 - x_2)(b - x_1 - x_2)(c - x_1 - x_2)} = \frac{dx_1}{dx_2} = \frac{k_1 (a_1 - x_1)}{k_2 (a_2 - x_2)} \quad (80)$$

Separation of the variables and integration, taking into account the initial condition of $x_1 = 0$ and $x_2 = 0$ at $t = 0$ gives

$$\ln \frac{a_1}{a_1 - x_1} = \frac{k_1}{k_2} \ln \frac{a_2}{a_2 - x_2}; \quad (81)$$

and hence

$$\alpha = \frac{k_1}{k_2} = \frac{\ln \dfrac{a_1}{a_1 - x_1}}{\ln \dfrac{a_2}{a_2 - x_2}} \quad (82)$$

We denote the fraction of the total conversion of a_1 by f_1 and the fraction of the total conversion of a_2 by f_2. Then $\frac{x_1}{a_1} = f_1$ and $\frac{x_2}{a_2} = f_2$. Substitution of these into Eqs. (81) and (82) gives

$$\left.\begin{aligned} &\text{a) } \ln \frac{1}{1 - f_1} = \frac{k_1}{k_2} \ln \frac{1}{1 - f_2}; \\ &\text{b) } \ln (1 - f_1) = \frac{k_1}{k_2} \ln (1 - f_2) \end{aligned}\right\} \quad (83)$$

and

$$\alpha = k_1 / k_2 = \frac{\ln (1 - f_1)}{\ln (1 - f_2)} \quad (84)$$

and

$$\delta = \alpha - 1 = \frac{\ln (1 - f_1) - \ln (1 - f_2)}{\ln (1 - f_2)} \quad (84a)$$

The connection between the specific content of a given isotope and the degree of conversion may be expressed in another way, using the quantities themselves rather than the logarithms. For this, Eq. (83b) is written as

$$\ln (1 - f_1) = \ln (1 - f_2)^{k_1/k_2}, \quad (85)$$

and hence

$$1 - f_1 = (1 - f_2)^{k_1/k_2} \quad (85a)$$

or

$$f_1 = 1 - (1 - f_2)^{k_1/k_2}. \quad (85b)$$

By means of this equation it is easy to derive an expression for the observed separation coefficient S. This coefficient, for isotope 1, may be defined as the fraction

$$S = \frac{\varkappa_X}{\varkappa_A}; \quad (86)$$

the denominator of this fraction is the ratio of the initial contents of isotopes 1 and 2

$$\varkappa_A = \frac{a_1}{a_2},$$

and its denominator is the ratio of the concentrations x_1 and x_2 of the same isotopes in the reaction product X at time t.

$$\varkappa_X = \frac{x_1}{x_2}.$$

These values of x_1 and x_2 correspond to f_1 and f_2. Simple transformation gives the expression

$$S = \frac{\varkappa_X}{\varkappa_A} = \frac{1 - (1 - f_2)^{k_1/k_2}}{f_1}. \quad (87)$$

For treatment of experimental data Eqs. (82) or (84) may be used to plot bilogarithmic graphs, α being calculated as the tangent of the angle of inclination of the straight line obtained.

In the most common case, when the tagged isotope content is negligible, it is possible to use the single conversion fraction f, found from the accumulation of the reaction products, and the ratio of the total or specific content of the tagged isotope in the products for different f to the total or specific content at complete conversion. For radioactive substances these values may be replaced by the number of counts over the background. Thus, in the present instance, with two independent directions of the reaction, with $\alpha = \frac{k_1}{k_2}$, the following equations are easily derived

$$S = [1 - (1 - f)^{k_1/k_2}] / f \quad (88)$$

or

$$\log \left[1 + (1 - S) \cdot \frac{f}{1 - f}\right] = \left(\frac{k_1}{k_2} - 1\right) \log (1 - f). \quad (89)$$

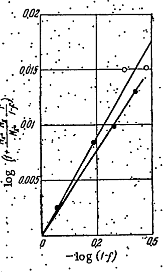


Fig. 95. Direct graphical determination of the isotopic coefficient δ for C^{12}/C^{13} from Eq. (89) for decarboxylation of mesitoic acid, after Bothner-By and Bigeleisen [61]. $\frac{N_{X^\circ} - N_X}{N_{X^\circ}} = 1 - S$. O) T = 61.2°C; ●) T = 92.0°C.

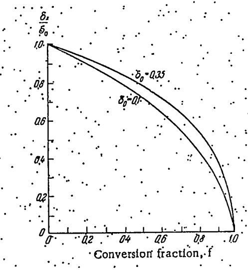
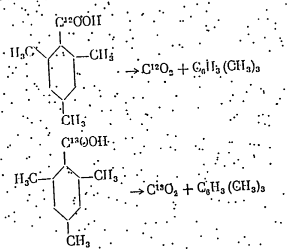


Fig. 96. Variation of the isotope effect $\delta = \alpha - 1 = \frac{k_1}{k_2} - 1$ with degree of conversion in molecular chemical reactions with different rate constants, after Bigeleisen [62].

The latter equation can be used for direct graphical determination of $\delta = \frac{k_1}{k_2} - 1$.

In illustration, Fig. 65, from the paper by Bothner-By and Bigelei en [61] on the C^{13}/C^{12} isotope effect for the decarboxylation of mesitoic acid, is shown



Some idea of the changes of isotopic composition due to values of α other than 1 is given by Fig. 96, which shows the course of the variations of $\frac{\epsilon}{\delta} = \frac{\delta_X}{\delta_0}$ where

$$\varepsilon = S - 1, \quad \delta = \frac{k_1}{k_2} - 1 = \alpha - 1 \quad \text{at} \quad k_1 > k_2 \text{ and } S > 1.$$

The attempts, sometimes met in the earlier papers, to identify α with S and δ with ϵ correspond to

$$\epsilon = \delta \tag{90}$$

and

$$\frac{\epsilon}{\delta} = 1 \tag{90a}$$

for any values of f.

In reality, as Fig. 96, calculated from the equation

$$\frac{\varepsilon}{\delta} = \frac{1 - (1 - f)(k_1/k_2 - 1)}{k_1/k_2 - 1} \cdot \frac{(1 - f)}{f} \tag{91}$$

shows, the ratio $\frac{\epsilon}{\delta} = 1$ only when f = 0. The value of this ratio decreases with increasing f, tending to 0 when f = 1. The shape of the curve depends on the magnitude of δ. With continuous conversion the ratio $\frac{\kappa_X}{\kappa_A}$ correctly represents the value of α only at the earliest stages of the decomposition. The error in δ reaches 10% (of the value determined) at 20% conversion for δ = 0.1 and at 25% conversion for δ = 0.35. The values of S for f ≦ 0.05, i. e., ≦ 5% can in most cases, without appreciable error, be used to characterize α and to determine δ.

In addition to the foregoing equations, based mainly on determinations of the isotopic contents of the conversion products, we quote a variation of the equation derived by Downes and Harris [63] for determination of the kinetic isotope effect from the isotopic composition of the unreacted residue, in relation to the isotope effect in formaldehyde conversion by the Cannizzaro reaction.

$$2CH_2O + OH^- \rightarrow CH_3OH + HCO_2^- . \tag{92}$$

Formaldehyde is the easiest of the reaction components to isolate and analyze. C^{14} was used in the work, and the equations directly contain the specific radioactivities of the original substance $[\Lambda] \equiv [CH_2O]$ at the start of the reaction, $r_0 = \left(\frac{\lambda[\dot{\Lambda}]}{[\Lambda]}\right)_0$, and at conversion fraction f, $\gamma_f = \left(\frac{\lambda[\dot{\Lambda}]}{[\Lambda]}\right)_f$.

The original differential equations for the indepent reactions of the tagged and untagged molecules are written as

$$-\frac{d[\Lambda]}{dt} = k\,[A]^n\,[B]^p\,[C]^q; \tag{93}$$

$$-\frac{d[\dot{\Lambda}]}{dt} = \dot{k}\,[\dot{A}]\,[A]^{n-1}\,[B]^p\,[C]^q; \tag{93a}$$

which are valid for low tracer isotope contents. In these conditions division of (93) by (93a) gives Eq. (80). One solution of this, analogous to (83) and (89), has the form

$$r_f = r_0(1 - f)^{\alpha - 1} = r_0(1 - f)^\delta \tag{94}$$

or

$$\ln r_f/r_0 = \delta \ln (1 - f). \tag{94a}$$

The slope of the bilogarithmic plot directly gives δ, where $\delta = \alpha - 1$, and $\alpha = \frac{\dot{k}}{k}$. Since C^{14} is heavier than C^{12}, $\alpha' = \alpha^{-1}$. In this way the following values were obtained:

$$\delta' = -0.0566 \pm 0.0012$$

and

$$\alpha' = 0.9434 \pm 0.0012.$$

These are the results for the simplest case of two parallel and independent reactions with the simplest stoichiometric coefficients and reaction orders, or with any stoichiometric coefficients and orders for a low content of the tagging isotope. More complex cases are also met in practice; for example, often more than one molecule of A is involved in the exchange, several possible directions of conversion may be possible for molecules of the same composition, several isotopic isomers of the molecules may be present, or, finally, the mechanism of the exchange may involve two or more steps. There are no difficulties in principle in the derivation of equations for such cases, but the resultant expressions are inconvenient, and usually attempts are made to select the conditions so as to simplify the problem, or to replace the determination of S for the total conversion by determinations of S for low degrees of conversion, identifying it with α. As an example, we shall consider the determination of $\alpha = S_0$ for the decomposition of ethyl bromide tagged in the carbon [64], discussed in Chapter IV.

The isotope effect was studied by variations of the C^{13} content. The decomposition, allowing for the presence of C^{13}, can be represented in the form of three parallel reactions:

$$\left.\begin{array}{ll} 1)\ CH_3CH_2Br \rightarrow CH_2 = CH_2 + HBr & k_1 \\ 2)\ CH_3\dot{C}H_2Br \rightarrow CH_2 = \dot{C}H_2 + HBr & k_2 \\ 3)\ \dot{C}H_3CH_2Br \rightarrow \dot{C}H_2 = CH_2 + HBr & k_3 \end{array}\right\} \tag{95}$$

Reactions 2) and 3) give isotopically indistinguishable molecules of ethylene $C^{13}H_2{=}CH_2$ but, in general, $k_2 \neq k_3$. Representing the concentrations of CH_3CH_2Br, $CH_3\dot{C}H_2Br$, and $\dot{C}H_3CH_2Br$ by a_1, a_2, and a_3, respectively, and the concentrations of C_2H_4 and $\dot{C}CH_4$ by x_1 and x_2, we can write for the start of the reaction

$$\frac{dx_1}{dx_2} = \frac{k_1 a_1^\circ}{k_2 a_2^\circ + k_3 a_3^\circ}. \tag{96}$$

With uniform distribution of C^{13} between CH_3 and CH_2Br $a_2^\circ = a_3^\circ$ and

$$\frac{x_1^\circ}{x_2^\circ} = \frac{a_1^\circ}{a_2^\circ}\left(\frac{k_1}{k_2+k_3}\right) \tag{97}$$

The separation coefficients S_0 at 0% decomposition, which is the required value of α, can be written as

$$S_0 = \frac{x_1^\circ}{x_2^\circ}\left(\frac{a_2^\circ + a_3^\circ}{a_1^\circ}\right) = \frac{x_1^\circ}{x_2^\circ}\left(\frac{2a_2^\circ}{a_1^\circ}\right) = \frac{2k_1}{k_2+k_3} = \alpha. \tag{98}$$

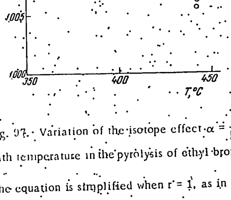


Fig. 97. Variation of the isotope effect $\alpha = \frac{2k_1}{k_2 + k_3}$ with temperature in the pyrolysis of ethyl bromide [64].

Direct experimental determination by combustion of ethylene in CO_2 followed by mass spectrometry of the latter gives not S_0 but S_f, for the final decomposition fraction f; this we shall denote simply by S.

A relationship between these two quantities, for a low content of C^{13}, may be derived by the methods used in the analysis of the preceding simpler case, in the form

$$S_0 = \alpha = 2k\,\frac{\ln(1-f)}{\ln\left[1 - \frac{k(1+r)}{L}\,\frac{f}{S}\right]} \tag{99}$$

In this expression

$$k = \frac{k_2^2 + k_3^2}{(k_2+k_3)^2};\quad L = \frac{k_2 + rk_3}{k_2+k_3} \text{ и } r = \frac{a_3^\circ}{a_2^\circ}.$$

The equation is simplified when r = 1, as in that case L = 1.

$$S_0 = 2k\,\frac{\ln(1-f)}{\ln\left[1 - 2k\frac{f}{S}\right]} \tag{100}$$

By the statistical theory $k_2 - k_3$ cannot exceed 0.02. With such small differences we may take, without any great error, $k = \frac{1}{2}$, and so reduce Eq. (100) to the final very simple form (100a) used for the calculations

$$S_0 = \alpha = \frac{2k_1}{k_2+k_3} = \frac{\ln(1-f)}{\ln(1-f/S)} \tag{100a}$$

Table 95, Chapter IV, gives the values of f, S, and S_0 found for different temperatures (see also Fig. 97).

§ 10. Kinetics of Isotopic Exchange with Superposition of Processes of Different Types

The search for general solutions in the kinetics of isotopic exchange with the superposition of complications of different kinds has so far not been very successful. Mention should be made of the work of Sheppard [65], who used a matrix calculation method to investigate the number of types of tagged molecules necessary to obtain all the partial kinetic exchange constants for complex systems, and who used the analogy with diffusion equations to derive the general kinetic equations.

Owing to the rejection of the explicit use of mathematical statistics, the results obtained by these authors even for a system with a small number of exchanging species are obscure. Their proposed electric model method is promising. Because of the lack of practically convenient general solutions, kinetic analysis in presence of various complicating factors is reduced as much as possible to the simpler cases discussed in Chapter II and in §6 of this chapter. This can be illustrated by the following example.

1. Isotopic exchange of F_2 with halogen fluorides and hydrogen fluoride.

Assuming both atoms in the fluorine molecule and the n fluorine atoms in the CF_n molecule kinetically identical, Adams, Bernstein, and Katz [66] determined R for the exchange of radioactive fluorine F^{18} by means of the modified Eq. (36) of Chapter II.

$$Rt = -2.3\,(2n\,[A][B])/(n\,[A] + 2[B])\log(1 - F).$$

For ClF_3, BrF_5, and HF with increasing $[CF_n] \equiv [A]$ R passes through a maximum, and with increasing $[F_2] \equiv [B]$ it increases almost linearly. This is the result of a Langmuir type of displacement of adsorbed fluorine by fluoride from the walls of the nickel vessel, at which the exchange predominantly occurs. Hence $R_{obs} = R_{heterog} + R_{homog}$, where $R_{heterog} = k_1 a_1 a_2 [A][B] / \{1 + a_1 [A_2] + a_2 [A_2]\}$, and $R_{homog} = k_2 [B]$, which takes homogeneous dissociative exchange into account; a_1 and a_2 are the adsorption coefficients for fluorine and fluoride, and k_1 and k_2 are the rate constants. A similar equation is applicable to the exchange of F_2 and IF_7. Thus, despite the existence of two exchange paths and the participation of up to nine fluorine atoms in the exchange, the kinetics is satisfactorily described by the equations of Chapter II.

In the exchange kinetics of radioactive isotopes the superposition of radioactive disintegration must often be taken into consideration. With such long-lived isotopes as C^{14} or T, the resultant concentration changes may be neglected in experiments of normal duration. On the other hand, in chemical investigations with isotopes with half-lives of 1 minute or less, radioactive disintegration is the main cause of changes in the concentrations of the tagged atoms. Against the background of this disintegration investigation of transfers caused by isotopic exchange or chemical reactions is so difficult that short-lived isotopes are used as tagged atoms only in isolated special cases, such as the emanation method.

The magnitude of the complications is determined by the ratio of the half-exchange time $t_{1/2}^{exch}$ to the radioactive half-life $\tau_{1/2}^{disint}$:

$$\text{when } \tau_{1/2}^{disint} \gg t_{1/2}^{exch} \tag{101}$$

disintegration may be ignored:

$$\text{when } \tau_{1/2}^{disint} \ll t_{1/2}^{exch} \tag{101a}$$

the use of the isotope for investigations of exchange is impossible; if $\tau_{1/2}^{disint}$ and $t_{1/2}^{exch}$ are of the same order of magnitude, the isotope may be used, but the effect of the disintegration must be taken into account.

If the radioactive isotope does not form new radioactive products by disintegration and does not contain other isotopic or isomeric radioactive forms, the isotope content at any instant can be calculated from the half-life or the decay constant λ, which are in the relationship

$$\lambda = \frac{0.693}{\tau_{1/2}}, \tag{102}$$

The concentration of a radioactive isotope, present in any chemical, aggregative, or physical state,* varies with time according to the simple exponential law

$$[\dot{M}]_t = [\dot{M}_0]\,e^{-\lambda t} = [\dot{M}_0]\,e^{-\frac{0.693}{\tau_{1/2}}} \tag{103}$$

By means of this formula all the measured radioactivities of the samples can be referred to one particular time. The introduction of corrections may be avoided by comparison with a standard specimen of the same isotope in the same chemical form. Sometimes it is preferable to introduce a direct correction for disintegration into the kinetic equation. For example, Koskoski, Dodson, and Fowler [67], who studied the isotopic exchange of bromide ions with α-bromopropionic acid in aqueous solutions, successfully used the following kinetic equation to represent the rate of formation of tagged organic halide:

---

* Apart from nuclear excitation, which cannot be induced by chemical processes.

$$\frac{d[\mathrm{R\dot{B}r}]}{dt} = k_1[\mathrm{RBr}][\mathrm{\dot{B}r}^-] - k_2[\mathrm{R\dot{B}r}][\mathrm{Br}^-] - \lambda[\mathrm{R\dot{B}r}] - k_3[\mathrm{R\dot{B}r}]. \qquad (104)$$

The first two terms of the right-hand side of the equation represent the changes in the concentration of tagged bromide caused by isotopic exchange in the forward and reverse directions, the third term takes into account the decrease of tagged bromide concentration caused by radioactive disintegration, and the last term indicates the subsidiary chemical hydrolysis reaction

$$\mathrm{R\dot{B}r} + 2\mathrm{H_2O} \rightarrow \mathrm{ROH} + \mathrm{H_3\overset{+}{O}} + \mathrm{Br}^-. \qquad (105)$$

Solution of this equation, when ρ_{Br} is small, gives the following expression for the exchange rate constant k_1:

$$k_1 = \frac{1}{[A]}\,\frac{t}{[B]}\ln\left[1-\gamma\frac{[A]+[B]}{[A]_t}\right], \qquad (106)$$

where [A] and [B] are the initial concentrations of RBr and Br^- ions; $[A]_t = [A]e^{-k_3t}$ is the concentration of RBr at time t, $\gamma = \gamma(t)$ is the fraction of the total radioactivity in the organic bromide. By the use of γ, λ vanishes from this equation, since the distribution of radioactivity between different chemical species does not change as the result of disintegration. Table 102 shows that Eq. (106) is fairly satisfactory.

TABLE 102

Results of Two Experiments of Koskoski *et al.* on the Kinetics of Bromide Ion Exchange at 100°C [67]

Experiment No.	t, min.	$[\mathrm{Br}^-]$	$[\mathrm{RBr}^-]$	γ	$k_1 \cdot 10^3$
1	10	0.0397	0.0301	0.101	6.4
	20	0.0411	0.0287	0.167	6.2
	30	0.0419	0.0272	0.216	6.4
	40	0.0430	0.0260	0.241	6.2
	50	0.0438	0.0254	0.262	6.0
	60	0.0453	0.0241	0.282	5.7
2	15	0.00406	0.0270	0.141	6.3
	30	0.00669	0.0253	0.236	6.2
	45	0.00776	0.0232	0.294	6.0
	60	0.00900	0.0220	0.366	6.5

Note. The experiments were performed in solutions containing 1.014 N H_2SO_4. In Experiment 1, [A] = 0.0318 N and [B] = 0.0376 N; in Experiment 2, [A] = = 0.0292 N and [B] = 0.00294 N.

In this investigation the solutions of radioactive sodium bromide, prepared from neutron-irradiated butylene bromide, were kept for 48 hours or longer before the experiments. This greatly reduced the initial activity, but also led to practically total disappearance of the radioactive Br^{80} isomers. It was therefore possible to use a single value of λ for radioactive disintegration in the calculations, and the initial equation was greatly simplified. It should be pointed out that the magnitude of the correction introduced by the decay of 39-hour radiobromine in experiments lasting 1 hour is very small, and it could have been neglected. The final expression for k_1 does not contain λ (if γ is used), as the disintegration changes the $\mathrm{\dot{B}r}$ contents in the bromide ions and the organic bromide equally. In analogous prolonged experiments with radioactive iodine I^{128}, with $\tau_{1/2}$ = 30 minutes, changes of $[\mathrm{\dot{I}}^-]$ and $[\mathrm{R\dot{I}}]$ due to disintegration would be an effect of the first kind, but even in this case λ would not enter the final equation in explicit form.

The above derivation and the resultant equation are not applicable to "young" radiobromine, which consists of a mixture of 4.5-hour Br^{80} with its isomeric 18-minute product and 39-hour radiobromine Br^{82}. The proportions of these three radioactive forms depend on the duration of the preliminary neutron irradiation and on the time which elapses from the end of the irradiation. More complex expressions would have to be introduced into the original differential equation for calculation of the changes of RBr caused by disintegration.

A second, more important complication is caused by the differences in the radiations emitted by these three radiobromines. 4.5-hour bromine emits only internal conversion electrons and soft γ-radiation with predominant energies of 0.049 and 0.037 Mev; 18-minute bromine emits energy-rich electrons with maximum energy of about 2 Mev, with small admixture of 1 Mev positrons and γ-radiation of about 0.5 Mev; finally, 39-hour bromine emits electrons with maximum energy of 0.465 Mev, and a complex spectrum of γ-radiation with energies from 0.553 to 1.317 Mev [66]. Because of this, not only the observed decay rate constants, but the nature of the ionizing radiation changes with time. The sensitivity of any counter varies for different types and energies of radiation, and the same number of disintegrations of different radioactive forms will, under equal conditions, give different numbers of initial pulses.

The most sensible method for the avoidance of such complications is the use of a comparison standard prepared from the same initial portion of radioactive material. It is obvious that the standard and the specimens compared with it must be measured in the same chemical and physical state, and identical conditions must be scrupulously maintained in the radioactivity measurements.

This concludes the chapter on complicated isotopic exchange. The kinetics of the redistribution of isotopes in complex chemical reactions has not been considered. This gap is partly filled by the discussion of M. B. Neiman's kinetic isotope method in §4, Chapter VI. The types and examples of complications given in Chapter V give an adequate idea of the importance and the diversity of such effects in homogeneous systems. For heterogeneous systems we confined ourselves to a consideration of cases to which the kinetic analysis methods used for homogeneous systems may be applied. Heterogeneous exchange has its specific characteristics. In particular, processes of material transfer to the interfaces are superposed on isotopic exchange and chemical reactions. Consideration of these lies outside the scope of the present monograph.

LITERATURE CITED

[1] S. Z. Roginsky, Bull. Acad. Sci. USSR, Div. Phys.-Math. Sci. 5, 601 (1940).

[2] O. Myers and R. Prestwood, in Radioactivity Applied to Chemistry, edited by Wahl and Bonner, Moscow, Foreign Lit. Press (1954).

[3] S. Z. Roginsky, in Symposium on Isotopes in Microbiology, Moscow, Acad. Sci. USSR Press (1955).

[4] S. Z. Roginsky, Proc. Acad. Sci. USSR, 100, No. 5, 393 (1955).

[5] B. V. Makarov, B. A. Rodin, and N. M. Emanuel, Kinetics of Chemical Reactions, Lithographed course of lectures by Prof. S. Z. Roginsky, Leningrad Industrial Institute (1939).

[6] S. Z. Roginsky, Progr. Phys. Sci. 11, 805 (1931); L. S. Kassel, Kinetics of Homogeneous Gas Reactions, Moscow, United Sci.-Tech. Press (1937).

[7] N. M. Dykhno and A. I. Shatenshtein, J. Phys. Chem. 28, 14 (1954).

[8] V. R. Kalinachenko, Dissertation, Karpov Inst., Moscow (1955); Ya. M. Varshavsky and A. I. Shatenshtein, Proc. Acad. Sci. USSR 91, 577 (1953); A. I. Shatenshtein and E. A. Izrailevich, J. Phys. Chem. 28, 3 (1954).

[9] N. E. Brezhneva, S. Z. Roginsky, and A. I. Shilinsky, Acta Physicochim. URSS 6 No. 5, 744 (1937).

[10] B. A. Kazansky and G. V. Bykov, in Symposium, A. M. Butlerov, Selected Papers in Organic Chemistry, p. 527, Moscow, Acad. Sci. USSR Press (1951).

[11] J. W. Baker, Tautomerism, Moscow, United Sci.-Tech. Press (1937). L. Fieser and M. Fieser, Organic Chemistry, Moscow, Foreign Lit. Press (1949).

[12] A. N. Nesmeyanov and I. F. Lutsenko, Bull. Acad. Sci. USSR, Div. Chem. Sci. 63 (1947); Proc. Acad. Sci. USSR 59, 707 (1948).

[13] A. N. Nesmeyanov and V. A. Sazonova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 422 (1949).

[14] A. N. Nesmeyanov, V. A. Sazonova, and E. B. Landor, Proc. Acad. Sci. USSR 63, 395 (1948).

[15] A. N. Nesmeyanov, Annals Moscow State Univ. 132, 5 (1950).

[16] A. N. Nesmeyanov and M. I. Kabachnik, Symposium; Problems of Chemical Kinetics, Catalysis, and Reactivity, Moscow, Acad. Sci. USSR Press, p. 644 (1955).

[17] K. H. Meyer, Ann. 380, 212 (1911); K. H. Meyer and P. Hoppelmeier, Ber. 44, 2718 (1911); K. H. Meyer, Ber. 45, 2843 (1912); 47, 826 (1914).

[18] C. K. Ingold, "Structure and mechanism in organic chemistry," 535-536, New York, 1953.

[19] E. H. Usherwood, J. Chem. Soc. 123, II, 1717 (1923); E. H. Ingold, J. Chem. Soc. 125, I, 1319 (1924).

[20] A. E. Chichibabin et al., J. Russ. Chem. Soc. 53, 193, 213 (1921); 58, 400, 406, 421 (1926), etc.

[21] K. Kwart, L. P. Kuhn, and E. L. Bannister, J. Am. Chem. Soc. 76, 5998 (1954).

[22] C. K. Ingold and C. L. Wilson, Z. Elektrochem. 44, 62 (1938).

[23] A. I. Brodsky, Isotope Chemistry, Moscow, Acad. Sci. USSR Press (1952).

[24] O. Reitz, Z. Phys. Chem. A 179, 119 (1937).

[25] G. P. Miklukhin, J. Phys. Chem. 21, 987 (1947).

[26] P. Goldfinger and W. Lasareff, C. r. 200, 1671 (1935); M. M. Slutskaya, Zh. M. Shershever, and A. I. Brodsky, J. Phys. Chem. 6, 1437 (1935).

[27] G. P. Miklukhin, Doctorate Dissertation, Inst. Phys. Chem., Acad. Sci. Ukrainian SSR, Kiev (1953).

[28] H. Erlenmeyer and H. M. Weber, Helv. chim. acta 21, 863 (1939).

[29] A. M. Butlerov, J. Russ. Chem. Soc. 9, 38 (1877); Works, Vol. I, Moscow, Acad. Sci. USSR Press, p. 322 (1953).

[30] M. I. Kabachnik, Symposium, Problems of Organic Reaction Mechanisms, Kiev, Ukrainian SSR Press, p. 126 (1954).

[31] L. Knorr, Ann. 306, 332 (1899).

[32] W. Hückel, Theoretical Principles of Organic Chemistry, Moscow, Foreign Lit. Press (1955).

[33] A. N. Nesmeyanov, V. A. Sazonova, and E. I. Vasilyeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 78 (1952).

[34] S. Z. Roginsky, Ukrain. Chem. J. 22, 24 (1956).

[35] V. Smirnov, Course of Higher Mathematics, Part II; E. Kamke, Handbook of Ordinary Differential Equations, Moscow, Foreign Lit. Press, p. 415 (1951).

[36] M. Curie, Radioactivity, Moscow-Leningrad, State Tech. Press, p. 177 (1947).

[37] S. Z. Roginsky, Progr. Chem. 9, 1241 (1940).

[38] C. Kemball, Proc. Roy. Soc. A214, 413 (1952).

[39] S. G. Hindin, G. A. Mills, and A. G. Oblad, J. Am. Chem. Soc. 77, 538 (1955).

[40] C. Kemball, Proc. Roy. Soc. A207, 539 (1951).

[41] S. G. Hindin, G. A. Mills, and A. G. Oblad, J. Am. Chem. Soc. 73, 278 (1951).

[42] J. W. Otvos, D. P. Stevenson, C. D. Wagner, and O. Beck, J. Am. Chem. Soc. 73, 574 (1951).

[43] R. Anderson and C. Kemball, Proc. Roy. Soc. A226, 472 (1954).

[44] G. C. Bond and J. Turkevich, Trans. Far. Soc. 50, 1335 (1954).

[45] A. I. Brodsky, Progr. Chem. 23, 614 (1954).

[46] Ya. A. Fialkov and Yu. P. Nazarenko, Proc. Acad. Sci. USSR 100, 719 (1955).

[47] D. I. Mendeleev, J. Russ. Chem. Soc. 2, 275 (1870). D. I. Mendeleev, Works, Vol. 25, p. 686.

[48] A. I. Brodsky and R. K. Eremenko, Proc. Acad. Sci. USSR 95, 539 (1954).

[49] J. A. Christiansen and W. Drost-Gansen, Nature 164, 759 (1949).

[50] A. H. Aten, Jr., J. Am. Chem. Soc. 74, 3706 (1952).

[51] A. Fava, Gazz. Chim. Ital. 83, 87 (1953).

[52] S. Z. Roginsky, Adsorption and Catalysis at Heterogeneous Surfaces, Moscow, Acad. Sci. USSR Press, (1948).

[53] S. Z. Roginsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1, 14 (1945).

[54] V. I. Levin, Progr. Chem. 17, 174 (1948); Problems of Kinetics and Catalysis 7, 205, 297 (1949).

[55] O. M. Todes and A. K. Bondareva, J. Appl. Chem. 21, 693 (1948); O. M. Todes, A. K. Bondareva, and G. A. Khachkuruzov, Problems of Kinetics and Catalysis 7, 263 (1949).

[56] M. I. Temkin and V. G. Levich, J. Phys. Chem. 20, 1441 (1946). M. I. Temkin, Problems of Kinetics and Catalysis 6, 154 (1949).

[57] S. Z. Roginsky and O. M. Todes, Acta Physicochimica URSS 21, 519 (1946). Problems of Kinetics and Catalysis 7, 248 (1949).

[58] G. M. Harris, Trans. Far. Soc. 47, 716 (1951).

[59] C. A. Bunton, E. A. Halevi, and D. R. Llewellyn, J. Chem. Soc. 4913 (1952).

[60] C. A. Bunton, D. P. Craig, and E. A. Halevi, Trans. Far. Soc. 51, 196 (1955).

[61] A. A. Bothner-By and J. Bigeleisen, J. Chem. Phys. 19, 755 (1951).

[62] J. Bigeleisen, Science 110, 14 (1949).

[63] A. M. Downes and G. M. Harris, J. Chem. Phys. 20, 196 (1952).

[64] H. Friedman, R. E. Bernstein, and H. E. Gunning, J. Chem. Phys. 23, 109, 1722 (1955).

[65] C. W. Sheppard, J. Appl. Phys. 19, 70 (1948); C. W. Sheppard and A. S. Householder, Ibid. 22, 510 (1951).

[66] R. Adams, R. B. Bernstein, and J. J. Katz, J. Chem. Phys. 22, 13 (1954). Ibid 23, 1622 (1955).

[67] W. Koskoski, R. Dodson, and R. D. Fowler, J. Am. Chem. Soc. 63, 2149 (1941).

CHAPTER VI

MAIN FIELDS OF APPLICATION AND DEVELOPMENT PROSPECTS OF ISOTOPE METHODS IN CHEMICAL KINETICS

§ 1. Leading Problems in Chemical Kinetics

Chemical kinetics originated at the end of the last century as a small section of physical chemistry dealing with the rates of thermal chemical processes (see Table 104). In the 1920's its scope began to expand and it showed a tendency to develop into a principal division of theoretical chemistry, on a level with chemical thermodynamics or the chemical structure of matter.

In this large new division, description of the course of thermal chemical processes with time gradually became only one, and not the most important, problem. Even in the attack upon this problem the leading positions were occupied by such new methods as calculations of absolute reaction rates with the aid of statistical physics and wave mechanics, the use of the theory of regimes, and of chain reactions. The leading position in chemical kinetics became occupied by determinations of the true stage mechanisms of chemical reactions, including the elementary chemical steps. In consequence many theoretical questions which were formerly considered in organic and inorganic chemistry without any connection with physical chemistry, entered the scope of the latter and became the objects of joint study by chemists and physicists of different specializations. In future, the boundaries between the different chemical science in this field will become even less distinct owing to the inclusion of chemical kinetic in the attack on the complex problem of the reactivity of matter.

As a result of elucidation of the nature of the quantitative coefficients which appear in the expressions for the rate constants for simple reactions, and of the determination of several types of mechanisms widely met in chemical kinetics, differentiated quantitative characterization of reactivity has become possible for the first time. In consequence of this, and of the brilliant successes of the electronic theory of chemical structure, a transition from qualitative and semi-empirical relationships to quantitative laws began in this central problem of theoretical chemistry. To accelerate this transition it is primarily necessary, using the modern and improved research methods, to study the true primary stages and intermediate products in as many individual chemical reactions of different types as possible. Further, the theory of absolute reaction rates should be used in studies of the relationship between directions, elementary mechanisms, and rates, on the one hand and chemical composition and structure of the reactants on the other. For this, the results of investigations of the structure of molecules and crystals and of their energy levels must be used systematically and directly in the development of a theory of chemical processes.

Only thermal reactions were studied in the old chemical kinetics. Chemical processes induced by light were studied in photochemistry; those induced by an electric current, in electrochemistry. Both photochemistry and electrochemistry developed without any direct connection with chemical kinetics. During the last few decades there has been a convergence of the individual physicochemical disciplines for studying chemical processes induced by different external agents, and the outlines of a future chemical kinetics, combining all that is known of chemical processes in different conditions and forms, began to appear clearly. Chemical reactions involving thermal energy only will form one of the parts of this "larger kinetics." Electrochemical, radiochemical, and mechanochemical processes will enter it on an equal basis. A classification of chemical reactions according to the forms of energy which induce the chemical processes, with indications of the main primary active forms, is given in Table 103.

TABLE 103

Classification of Chemical Reactions According to the Predominant Forms of Activating Energy

Group	Form of activating energy	Notes
Class I. Thermal chemical reactions		
	Thermal energy fluctuations, transmitted by collisions between molecules, and by vibrations within molecules and crystals	
Class II. Radiochemical reactions		
1. Photochemical reactions	Light photons in the visible and ultraviolet regions of the spectrum	Sometimes also light from the near infrared region
2. X-ray and γ-ray chemical reactions	Photons of hard x-rays and γ-ray electromagnetic radiations	Radiochemical reactions in the narrow sense of the term
3. Reactions induced by corpuscular radiation	Kinetic energy of rapidly moving particles, electrons, and ions, usually several orders of magnitude greater than the rupture energy of ordinary chemical bonds.	
Class III. Electrochemical processes		
1. Chemical reactions in different forms of electric discharge	Electrical energy supplied into the discharge space	In some forms of discharge (for example, in arc or condensed discharge) the super-high temperature may be of independent importance
2. Electrochemical reactions in the narrow sense of the term	Electrical energy supplied to the electrolyte at its boundary with the electrode	The primary process always reduces to loss of electrons at the anode or gain of electrodes at the cathode
Class IV. Mechanochemical processes		
1. Piezochemical reactions	Mechanical energy of isothermal and adiabatic compression	Appreciable piezochemical effects begin to appear at thousands of atmospheres.
2. Acoustic reactions	Energy of ultrasonic, much less frequently ordinary sonic vibrations	
Class V. Chemical reactions of "hot atoms"		
Chemical reactions accompanying nuclear processes.	Recoil energy of atoms in nuclear processes	

All chemical kinetics in the traditional sense of the term, together with catalysis and chemical reactions of solids, comprises only one of five classes, and moreover it is not divided into narrower groups. Some of the other classes, such as that of radiochemical reactions, cover wider ranges of phenomena than the first. Of all the forms of energy, only thermal energy is met without the others in chemical kinetics. All the others act with the simultaneous obligatory participation of thermal energy. Therefore, even when heat is not the main activating agent, the heat content of the system and its associated temperature remain very important factors. Since chemical reactions are accompanied by changes of heat content, the rate of heat removal and the associated thermal conditions of chemical reactions have very general importance. Their theory is included in macroscopic kinetics, which also covers the role of mass transfer, including diffusion, in chemical kinetics. Macroscopic kinetics, which has arisen almost entirely during the past 20 years, is one of the practically most important divisions of chemical kinetics. At the present time there are few kinetic investigations in which its results can be ignored and macrokinetics analysis of the process conditions avoided.

Originally, only homogeneous reactions in aqueous solutions were studied practically in chemical kinetics. At the start of the present century chemical kinetics began to converge with the older province of heterogeneous catalysis, and the kinetics of homogeneous gas reactions began to develop. This was followed by the beginning of investigations of the kinetics of chemical reactions of solids without solution or fusion. The scope of modern chemical kinetics includes both homogeneous reactions in any state of aggregation, and heterogeneous reactions for any combination of phases and any types of interphases. With regard to phases, chemical thermal reactions have been most fully studied; a concise classification based on this principle is given in Table 104. The same phase types are also met among reactions induced by other forms of energy, but here they have been studied less fully.

TABLE 104

Phase Classification of Thermal Reactions

Subclasses according to homogeneity	Type of process by state of aggregation and phase conditions	Notes
	I. Chemical thermal reactions	
Homogeneous reactions	1. Homogeneous gas reactions 2. Homogeneous reactions in liquids 3. Homogeneous processes in flames and explosion zones	With and without homogeneous catalysts
Heterogeneous reactions at solid surfaces	1. Chemical adsorption 2. Contact gas reactions 3. Contact reactions in liquids	Heterogeneous reactions at liquid surfaces are omitted, having been little studied in ordinary kinetics
Exchange chemical reactions of solids	1. Phase transformations in crystal lattices 2. Chemical reactions of solids not involving gases or solutions 3. Chemical reactions of solids involving gases and solutes 4. Chemical reactions of colloidally disperse systems	First type of process is close to crystallization, which is not included in the classification The third type is close to the solution of gases in solids
	II. Macroscopic thermal reactions	
Heat transfer	Transfer of energy by heat conduction and radiation	Heat and mass transfer may be intensified by mechanical energy (mixing, agitation, turbulization, convection
Mass transfer	Mass transfer by diffusion and flow	

In extension of the scope of problems covered by chemical kinetics the continuous extension of the range of external conditions in which chemical processes are effected has played an important part. For example, the temperature range covers thousands of degrees, from the boiling point of hydrogen (20.5°K) to the temperatures of the hot forms of electric discharge (10,000°K and higher). The ratio of the extreme temperatures $T_{max} : T_{min}$ reaches 500. The pressure range covered by kinetics is still wider — from millionths of a millimeter of mercury to hundreds of thousands of atmospheres. The ratio of extreme pressures $p_{max} : p_{min}$ is about 10^{14} (!). There have also been great increases in the range of solvents used in kinetic studies, in the selection of the reactants studied, catalysts, and types of processes; the energy range of the acting electromagnetic and corpuscular radiations has been considerably extended.

The chemical behavior of substances is influenced considerably by their nature, the form and potential of the acting energy, the presence and character of overt or covert catalysts, presence and nature of solvents, and phase conditions. This creates a boundless diversity of chemical processes, which, in one aspect, are studied in the chemical sciences based on the compositions of the substances in question (organic, inorganic, and biological chemistry); in another aspect, in sciences distinguished by the direction of their applications (technical chemistry, chemistry of structural materials, pharmaceutical chemistry); and in a third aspect, in physical (theoretical) chemistry and its branch of chemical kinetics.

In the last few decades, in addition to the accumulation of enormous amounts of experimental material on the specific characteristics of chemical processes, some general properties have also emerged, which indicate the existence of general principles applicable to very many chemical systems. In the near future it is to be hoped that laws will be established which represent the influence of the factors listed above on the mechanism, direction, and rate of chemical processes. These general principles and laws should form the basis of a general theory of chemical processes which covers the latter in all their diversity. The development of this theory is the central task of modern chemical kinetics. Its accomplishment requires, on the one hand, the determination of accurate and reliable data on the mechanisms of the largest possible number of reactions of different types, to serve as the starting points for theoretical derivations; searches for new, as yet unknown types of elementary processes and new methods of influencing reactions are particularly important. On the other hand, it is important to discover new and deeper laws which, on the basis of the general laws of micromechanics and the theory of the structure of matter, and with regard to the particular mechanisms met in chemical kinetics, would combine into one entity all the chemical reactions of different classes, groups, and types, covering all their diversity.

We shall now discuss these general problems and attempt to determine the place of isotope methods in their solution.

§2. Isotope Methods for Studying Ordinary (Elementary) Chemical Reactions

a) Complex character and steps in chemical reactions

One of the most general characteristics of chemical reactions of all types and classes is their divisibility into simpler steps or stages. Processes consisting of one step are extremely rare; examples are the volume recombination of hydrogen atoms and the para–ortho conversion of molecular hydrogen in presence of paramagnetic substances. Even the heterogeneous recombination of hydrogen and the para–ortho conversion of hydrogen at surfaces of paramagnetic solids consist of at least three steps, because of the need for adsorption and desorption. In such processes as homogeneous or catalytic cracking of individual high-molecular hydrocarbons the number of elementary steps which must be considered in detailed analysis of the processes is counted in dozens. This is also true for the radiolysis of large molecules. The number of individual elementary reactions increases still more if the reaction involves not a single compound but a mixture of several or many compounds, or if several reagents act simultaneously on a single substance. The individual elementary reactions represented in an entire chemical process may be consecutive steps (stages) or may refer to different parallel conversions of the starting substances. A certain number, sometimes very large, of side reactions must be added to this. Definite steps may be repeated, making the process a chain reaction. The main process may be inhibited by side reactions which terminate the chain or decompose the main reaction products. One of the principal tasks of detailed experimental kinetic investigations of individual systems is to reveal all the elementary reactions concealed in the entire chemical process and to determine the true relationships between these elementary reactions. Another aspect of this same problem of analyzing a complex process into the simplest elementary chemical reactions is the identification of all the stable and unstable chemical species formed in the reaction, and determination of their functions and genetic relationships. The first task here is to establish which substances are intermediate forms and catalysts for each of the parallel directions of the process, and which do not take part in any of these directions but are side products. It is also necessary to know which of the steps of the whole process determine its rate under various conditions, and how the superposition and summation of the elementary reactions leads to the experimentally determined kinetic equations.

By comparison of experimentally established stage schemes for different reactions it is possible to detect the general principles on which a combined process is built from the elementary steps. The classification of elementary processes by types and determination of the laws of their combination into entire processes of different groups is one of the crucial theoretical problems of chemical kinetics.

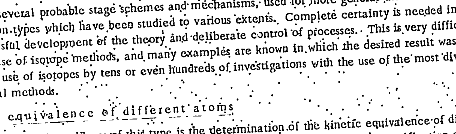
Usually one or several probable stage schemes and mechanisms, used for more general theoretical derivations, exist for reaction types which have been studied to various extents. Complete certainty is needed in these matters for the successful development of the theory and deliberate control of processes. This is very difficult to achieve without the use of isotope methods, and many examples are known in which the desired result was not achieved without the use of isotopes by tens or even hundreds of investigations with the use of the most diverse chemical and physical methods.

b) Tests for the equivalence of different atoms

One of the characteristic problems of this type is the determination of the kinetic equivalence of different atoms of the same element in a molecule. In some cases this constitutes a peculiar kinetic verification of accepted views on the structure of a particular compound, and in others, an investigation of the kinetic characteristics of atoms which cannot be predicted with sufficient certainty by the theory of structure and on general kinetic considerations. In investigations in which side factors are taken into account, the discovery of kinetic nonequivalence conclusively indicates the existence of differences in the valence states or positions of the atoms in the molecule, which significantly affect the reactivity of the element. Conversely, equivalence may be apparent, caused by reversible tautomeric intramolecular transformations, occurring at a rate greatly in excess of the rate of the reaction being studied. In such conditions the hidden rapid reversible reaction may be detected by varying the reaction conditions or by increasing the sensitivity of the method.

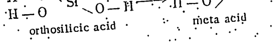
One method for studying chemical equivalence is the preparation of the compound in question by the successive introduction of atoms of different isotopes of the same element. Thus, in the formation of a compound AX_n, it is possible first to prepare AX_i, and then to introduce j atoms of $\overset{*}{X}$ into the molecule to give the compound $AX_i\overset{*}{X}_j$, where $i + j = n$. By studies of reactions in which not all the X atoms are involved simultaneously, the isotopic compositions of the products may be used to establish the equivalence or nonequivalence of the atoms in the molecule.

An instructive example is the investigation of the equivalence of the chlorine atoms in phosphorus pentachloride. This molecule in the gas and liquid phases is generally assumed to have the structure of a trigonal bipyramid [1] with a central phosphorus atom. In general, the chlorine atoms in such a bipyramid should be at two different distances from the P atom – one for the three atoms of the common base of the two pyramids (the equatorial atoms), and another for the two apical atoms. The crystal lattice of PCl_5 consists of positively charged



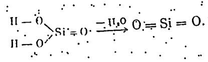
$[PCl_4]^+$ complex ions and negatively charged $[PCl_6]^-$ complex ions [2]. The bond forms between chlorine and phosphorus in these complexes are different. This suggests that the chlorine atoms in the pentachloride should be kinetically nonequivalent, but it is not clear whether this nonequivalence is sufficiently large to be detected and whether any intramolecular rearrangements occur which may destroy this distinction. The first study of this question was made by Koskoski and Fowler [3], who investigated the isotopic exchange of PCl_5 with Cl_2 in carbon tetrachloride with the use of short-lived Cl^{38}. They concluded that all five chlorine atoms were kinetically equivalent, but because of the difficulties in work with short-lived chlorine they could have easily missed slight differences. In view of this, Downs and Johnson repeated this work, using long-lived Cl^{36} as tracer, and with an improved technique for the separation of chlorine from PCl_5. They found that three chlorine atoms are exchanged rapidly and the other two considerably more slowly. It is probable that the equatorial atoms are exchanged rapidly and the apical atoms slowly [4]. By synthesizing PCl_5 from PCl_3 and Cl_2 of different isotopic composition, they observed another interesting manifestation of nonequivalence: the added chlorine accumulated predominantly in the rapidly exchanging equatorial part of the molecule. The structural interpretation of this observation is obscure [229]. Isotopic exchange studies with many metal halides showed the atoms to be equivalent. Some examples were given in Chapter III, and some of the results have been tabulated by Linnenbom [5]. However, in some cases the possibility of hidden nonequivalence, not detected because the analytical methods were too slow, is not excluded.

In general, the results obtained by means of isotopic exchange studies or investigations of the distribution of isotopes in chemical reactions agree with the modern theory of chemical structure. For example, the two sulfur atoms in thiosulfate, which contains in the $S_2O_3^{2-}$ anion one hexavalent and one bivalent sulfur atom [6] $S \cdot SO_3^{2-}$, are found to be nonequivalent. The iron atoms in the soluble complex compound $Fe^{III}Fe^{II}(CN)_6$, obtained by mixing solutions of inactive ferric chloride and potassium ferrocyanide with active iron, are nonequivalent. Ammonia precipitates inactive ferric hydroxide from the mixed solution [7, 8]. This is in full accordance with the data on the structure of the thiosulfate ion and of crystals of iron ferrocyanides. Experiments with radiocarbon have shown that individual carbon atoms strictly retain their positions in carbon chains and rings. Therefore the occasionally observed discrepancies between the results of kinetic investigations of the equivalence of atoms and the structural theory indicate the existence of additional undetected hidden transformations, which may also play an important part in ordinary chemical processes (see below). An interesting instance of equivalence, difficult to explain by the old structural theory, was found in studies of isotopic exchange of oxyacid anions. In the classical formulation of oxyacids, loss of water by ortho forms leads to appearance in the molecule, in addition to the original hydroxyl oxygen, of oxide oxygen linked by two bonds to the central atom.



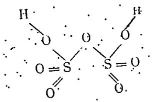
$$\underset{\text{orthosilicic acid}}{\begin{matrix}H-O\\H-O\end{matrix}\!\!>Si<\!\!\begin{matrix}O-H\\O-H\end{matrix}} \xrightarrow{-H_2O} \underset{\text{meta acid}}{\begin{matrix}H-O\\H-O\end{matrix}\!\!>Si=O} \qquad (1)$$

Further dehydration to acid anhydrides again gives strucures with only one type of oxygen atom, but this time of the oxide type



$$\begin{matrix}H-O\\H-O\end{matrix}\!\!>Si=O \xrightarrow{-H_2O} O=Si=O. \qquad (2)$$

In more complex cases the existence of three types of oxygen atoms must be assumed, as in pyrosulfuric acid



and its salts. With "fixed" bonds, models with two or three structural types of oxygen should contain kinetically nonequivalent atoms; this nonequivalence should be seen not only in isotopic exchange but in ordinary chemical reactions, in the form of deviations of the isotopic composition of the reaction products from equipartition in molecules tagged in definite atomic positions. Nevertheless, all the peripheral oxygen atoms are found to be completely equivalent kinetically in all the homogeneous reactions of oxygen exchange of acids and salts with one central atom in the anion, which have yet been studied. Similarly, no differences between hydroxyl and oxide oxygen can be detected with regard to position or bond strength by x-ray or optical investigations. This indicates a strictly symmetrical arrangement of all the nonperipheral* oxygen atoms, and their kinetic equivalence. In more complex compounds of the same type, containing two or more central acid-forming atoms, the indubitable distinction between the internal atoms of the oxygen bridges, linked simultaneously to the two acid-forming atoms and the remaining peripheral oxygen, is often not revealed in exchange. The contradiction between chemical structure and kinetic properties is resolved by the electronic theory of oxyacid anions. By this theory each central atom in the anion is surrounded by an electron octet, partial ionization of the chemical bonds between the central atom and oxygen assisting the approach of the octet to the inert gas structure [9, 10]. Similarly, the results of isotopic exchange studies indicate the complete equivalence of all the hydrogen atoms in the ammonium ion, etc.

---

* As in original – Translator.

The above examples demonstrate the significance of investigations of kinetic equivalence in elucidation of the chemical structure and reactivity of compounds. If the existence of atoms of a particular element, differing in structural positions or valence forms, in a compound is proved conclusively by the chemical structure of the molecule, or is established by isotopic exchange, another typical research problem arises: determination of the nature of the participation of different atoms of an element in a molecule in actual chemical reactions.

c) Determination of the kinetic roles of different atoms of a particular element in a process

Saponification and hydrolysis of esters.

In the saponification of esters according to the equation

$$R_1CO_2R_2 + H_2O \rightleftarrows R_1CO_2H + R_2OH \qquad (3)$$

the hydrolysis of the organic molecule may be regarded as occurring either at the O—R_2 bond, or at the C—O bond. In the first instance both oxygen atoms of the ester enter the acid, while the oxygen of water is joined to R_2 to give the alcohol. In the second instance one of the ester oxygen atoms is removed with the R_2 radical, and the alcohol formed should not contain oxygen from water. The latter will enter the carboxylic acid

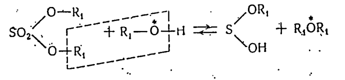
$$\left.\begin{array}{l} R_1CO-O\boxed{R_2 + H-O}H \rightleftarrows R_1-CO-OH + R_2OH \\ R_1-CO\boxed{O-R_2 + H}O-H \rightleftarrows R_1CO-OH + R_2OH \end{array}\right\} \qquad (4)$$

Polanyi and Szabo first showed that it is possible to decide between these two mechanisms by experiments on the hydrolysis of esters by water tagged with heavy oxygen isotopes (O^{18} and O^{17}). In hydrolysis of amyl acetate in an alkaline medium [11], these authors could not detect heavy oxygen in the isoamyl alcohol, but found it in acetic acid. Consequently, the reaction involves rupture of the acyl bond between oxygen and the acid residue, and not of the alkyl bond linking oxygen to the amyl radical

$$CH_3-CO\boxed{O-C_5H_{11} + H}\overset{*}{O}H \rightleftarrows CH_3CO\boxed{\overset{*}{O}H + H}OC_5H_{11} \qquad (4a)$$

By the detailed balancing principle, in the reverse esterification reaction the acyl oxygen bond should again be broken, with hydrogen removed from the alcohol hydroxyl, as shown by the broken lines in Equation (4a).

This method for determination of the location of bond cleavage was later used successfully by numerous workers in studies of the hydrolysis of esters of various organic and mineral acids. Three types of bond rupture were discovered: the acyl type described above, the alkyl type, and mixed. The type primarily depends on the strength of the acid and the acidity of the solution. The nature and structure of the alcohol also has a definite effect. Acyl rupture is found in the hydrolysis of γ-butyrolactone [12]. On the other hand, the formation of ethyl ether from diethyl sulfate proceeds entirely with cleavage at the alkyl radical [13]



(4b)

The acid hydrolysis of tertiary butyl acetate [14] is of the same type

$$CH_3COO\boxed{CMe_3 + H\overset{*}{O}}H \overset{H^+}{\rightleftarrows} CH_3CO_2H + H\overset{*}{O}CMe_3. \qquad (5)$$

Mention must also be made of the results obtained by N. I. Dedusenko and A. I. Brodsky [15], who established the position of bond rupture in the reaction of acetic anhydride with ethyl alcohol

$$CH_3CO-O|COCH_3 + H|\overset{*}{O}-C_2H_5 \rightleftarrows CH_3COO|H + C_2H_5\overset{*}{O}|OCCH_3. \qquad (6)$$

and by Blumenthal and Herbert [16], who showed that alkyl and acyl cleavage occur together in the hydrolysis of methyl orthophosphate.

In hydrolysis and esterification, the acyl type of cleavage predominates in alkaline and neutral media, and the alkyl type in acid media. The first mechanism is typical for esters of weak and moderately strong carboxylic acids with primary alcohols. This and other, finer relationships revealed the distinctions between the reactivity of a neutral ester molecule $R_1CO_2R_2$, typical at moderate and high pH values, and of the conjugate oxonium acid $[R_1CO_2HR_2]^+$ typical at low pH. As it is not possible here to discuss in detail other data on the mechanism of this group of reactions obtained by determinations of the position of bond rupture with the aid of heavy oxygen, we refer to an interesting analysis of these data in Ingold's monograph [10].

Reactions of polythionates

For our second example we consider in greater detail the reactions of thionic acids which were briefly mentioned in Chapter III, §10. Some workers have studied the distribution of radioactive sulfur in various reactions in di- and polythionic acids with various reagents containing sulfur. A detailed summary of A. I. Brodsky's data on the mechanism of these reactions, obtained by the use of sulfur-tagged compounds, is contained in a recent review article [17]. Studies of the distribution of radiosulfur in various reactions of formation and conversion of thionic acids revealed some interesting relationships; for example, atoms of bi- and hexavalent sulfur contained in thionic acids are not mutually converted in many reactions but retain their individuality. Hexavalent sulfur is always transferred together with oxygen, sometimes in the form of sulfate ions SO_4^{2-}, or as sulfite ions SO_3^{-}, or as SO_3, or as thiosulfate ions $(SSO_3)^{2-}$. In the first two instances $S^{II}-S^{VI}$ bonds are broken (sometimes with conversion of S^{VI} into S^{IV}) and in the last, for all thionates except trithionates, $S^{II}-S^{II}$ bonds. For example, according to Aten [18], the reductive decomposition of tetrathionate tagged in the hexavalent sulfur by means of sulfide, proceeds according to the scheme

$$\left[O_3\overset{*}{S}-S\,|\,S-\overset{*}{S}O_3\right]^{2-} \overset{2\ominus}{\curvearrowleft} + \; S^{2-} \longrightarrow 2S\overset{*}{S}O_3^{2-} + S \qquad (7)$$

while the hydrolysis of thiosulfate by water in presence of silver ions takes place according to the scheme

$$-\overset{*}{S}\,|\,SO_3^{2-} + 2Ag^+ + H_2O \rightarrow Ag_2\overset{*}{S} + SO_4^{2-} + 2H^+ \qquad (8)$$

etc.

Studies of thionate reactions with the aid of radiosulfur convincingly confirm the old theory of the structure of thionic acids and polythionates, which was advanced as long ago as 1870 by D. I. Mendeleev [19]. By this theory, thionic acids are sulfo-derivatives of the corresponding hydrogen sulfides. Thus, thiosulfate is H_2S in which one of the hydrogens is replaced by a sulfo-group, $HS-(SO_3H)$; tetrathionates are derived from hydrogen disulfide H_2S_2 in which both hydrogens are replaced by a sulfo-group or its salt, $(MeO_3S)-S-S(SO_3Me)$. As a rule, both hydrogens are replaced, and therefore polythionic acids, of any degree of complexity, usually contain only two hydrogen atoms and only two hexavalent sulfur atoms in their molecules. The molecular size is increased by lengthening of the sulfide chain with the sulfo-groups at its ends

$HO_3S-S-SO_3H$	$HO_3S-S-S-S-SO_3H$
trithionic acid	pentathionic acid

The presence of unbranched sulfide chains in such compounds, postulated by Mendeleev and disputed by other authors [20], is also confirmed.

Experiments with tagged sulfur have also shown that arsenious acid $As(OH)_3$, added as a catalyst in some syntheses of polythionates, acts as a peculiar carrier of sulfide sulfur atoms. These carriers bring about the formation and lengthening of the sulfide chains in the molecule [21].

§ 3. The True Genetic Relationships of Stable Molecules Which Participate and Appear in Complex Reactions

a) Oxidation reactions

The second typical problem in isotopic studies of chemical reactions is determination of the true genetic relationships of the various substances which appear in complex chemical reactions. It is of primary importance, in choosing between possible mechanisms of a complex process, to determine what is formed from what, even if only for the stable molecules which can be isolated. If the mechanisms are unknown or if the postulated schemes have been disproved, such determinations provide a reliable basis for establishing the correct mechanisms. We shall illustrate these potentialities of isotope methods by the example of the oxidation of hydrocarbons by molecular oxygen, which has been intensively studied by Soviet workers in recent years.

In these reactions, in addition to carbon dioxide and water, various organic oxygen-containing compounds are formed by incomplete mild oxidation. Secondary reactions which do not require oxygen, such as condensation, isomerization, pyrolysis, etc., occur at the same time. By variation of the external conditions and suitable choice of catalysts it is possible to obtain a predominance of particular oxidation products, but other stable products are always formed, even if only in small quantities, as well as various unstable intermediate products – radicals, peroxides, etc., observed or postulated by various authors. Table 105 gives a brief summary of some types of hydrocarbon oxidation, most of which are effected catalytically. The classification is based on the nature of the predominant reaction products. It does not include reactions known to require two or more molecules of oxygen-containing compounds.

Although it is not claimed that all the possible processes in this group of reactions are included, the seven types of reactions in Table 106 give some idea of their diversity. The classification into types is not particularly rigid. For example, in the formation of aldehydes from olefins, which has been included in the second type, intermediate formation of ortho-forms with two (or several) hydroxyls is possible, i. e., initial reactions of the 5th type. The latter, in turn, probably begin with reactions of the second or first types, etc.

Table 105 shows the formation of CO_2 and H_2O only in extensive oxidation, oxidative dehydrogenation, and cracking. In reality water is formed in reactions of nearly all types, and the number of molecules formed in each case exceeds the number of molecules of the main organic oxidation product. Simultaneously some carbon dioxide is always formed; often carbon monoxide is also obtained as a side product.

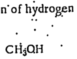
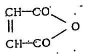
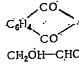
A comparison of the ease of oxidation of hydrocarbons and their oxygen derivatives showed that alcohols and aldehydes begin to be oxidized at lower temperatures [24]. In consequence, the theory of homogeneous [25] and heterogeneous [26] oxidation of hydrocarbons still contains oxidation mechanism schemes according to which the oxidation passes consecutively through all or nearly all the stable oxidation products with intermediate contents of oxygen. The formation of carbon dioxide is the last link in this chain. Even in the case of methane this results in a staircase reaction scheme with two or three intermediate steps

$$\begin{tikzcd} CH_4 \arrow[r] & CH_3OH \arrow[r] & CH_2O \arrow[r] \arrow[rr, bend right] & HCOOH \arrow[r] & CO_2 \end{tikzcd} \tag{9}$$

These steps are much more numerous for the more complex hydrocarbons, as the above sequence may occur consecutively for each carbon atom, and incompletely oxidized chains or rings may become detached, to react further with formation of carbon dioxide. The peroxide theory of oxidation [27] has not changed this fundamental idea. In some cases it has added further steps to the postulated sequences, and has changed them in others. The fundamental principle of a "staircase" with stable steps is also retained in many radical chain oxidation schemes, in which attempts are made to reconcile the old concepts with the inclusion of unstable compounds between the stable intermediate products. It was not possible to clarify these questions without the use of isotope methods, and for a long time controverises continued between supporters of the different viewpoints, without leading to a solution of the problem. As an example, we may mention the controversy between V. Ya. Shtern[28] and M. B. Neiman [29] on the mechanism of the homogeneous oxidation of hydrocarbons. To substantiate the stage mechanisms it is first necessary to establish the true genetic relationships between the stable substances present in a process. This was done for catalytic oxidation of hydrocarbons in a series of experimental investigations in our laboratory, in which the transformation directions of all the substances which appeared in the reaction were determined with the aid of carbon-tagged molecules.

TABLE 105

Types and Examples of Reactions of Hydrocarbon Oxidation by Molecular Oxygen

Substance oxidized	Main reaction product	Catalyst, notes.
	1. Oxygen addition	
$CH_2{=}CH_2 \begin{smallmatrix}\nearrow \\ \searrow\end{smallmatrix}$	 $CH_3{-}CHO$	Ag Possible reaction
2. Partial selective oxidation of hydrogen with introduction of one oxygen atom into the molecule without destruction		
CH_4	CH_3OH	Under high pressure without catalysts.
CH_4	CH_2O	Homogeneous catalysis, HBr
$C_6H_5{-}CH_3$	$C_6H_5{-}CHO$	V_2O_5; WO_3; MoO_3
$CH_2{=}CH{-}CH_3$	$CH_2{=}CH{-}CHO$	Cu_2O
3. Destructive oxidation with scission of the carbon skeleton and formation of two or more oxidized products		
$CH_3{-}CH{=}CH_2$	$CH_2O + CH_3CHO$	V_2O_5; MoO_3; WO_3
Paraffins; naphthenes	Fatty acids; alcohols	Without catalysts; with Na_2CO_3, stearates, and oleates of Mn, Zn, Co, etc. as catalysts
	4. Oxidative condensation	
CH_4	C_2H_2	Homogeneous at high temperatures
CH_4	C (black)	C autocatalysis; metals
5. Oxidation with formation of several OH, C=O, or COOH groups in one molecule		
Benzene		V_2O_5
Naphthalene		V_2O_5
$CH_3{-}CH{=}CH_2$	$CH_2OH{-}CHOH{-}CH_2OH$	Possible reaction
	6. Oxidative dehydrogenation and oxidative cracking	
$C_6H_{11}CH_3$	C_6H_6; CO_2; H_2O	E. g., cracking by Dubrovai's method [22, 23]
C_nH_{2n+2}	$C_kH_{2k} + C_iH_{2i+2}$; CO_2; H_2O	
7. Extensive oxidation with complete destruction of the hydrocarbon skeleton		
$\left.\begin{matrix} C_nH_{2n+2} \\ \text{Naphthalene} \end{matrix}\right\}$	CO_2, H_2O	Homogeneous combustion in burners and internal combustion engines. Contact oxidation over Pt; Pd, Cu; oxides of Cr, Ni, Mn; chromites and ferrites of Mg, Cu, Ni, etc.

The simplest of the reactions given in Table 105 is the direct addition of oxygen. As an example of reactions of this type, the oxidation of ethylene to ethylene oxide in presence of silver was studied. With good catalysts, only ethylene oxide, carbon dioxide, and water are formed in appreciable amounts below 400°C [30]. Above 500°C, formaldehyde may predominate in the products and formic acid also appears. In early work the following sequence was assumed for the formation of ethylene oxide

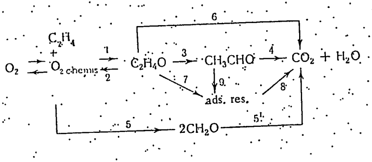
$$C_2H_4 \xrightarrow{O_2} C_2H_4O \xrightarrow{O_2} CO_2, \qquad (10)$$

all the carbon dioxide being formed from ethylene oxide. This old view, which still has its supporters [31] is now contrasted with the parallel independent formation of carbon dioxide and ethylene oxide [32]

$$\begin{aligned} &C_2H_4 \xrightarrow{O_2} C_2H_4O \\ &C_2H_4 \xrightarrow{O_2} (X?) \xrightarrow{O_2} CO_2. \end{aligned} \qquad (11)$$

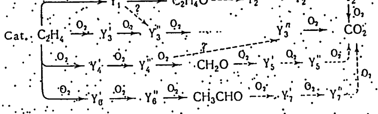
The two viewpoints are reconciled in Twigg's scheme [33], in which the simultaneous formation of carbon dioxide from ethylene oxide according to Scheme (10) and, without involving C_2H_4O, according to Scheme (11) is assumed. Catalytic oxidation of mixtures of ordinary ethylene with ethylene oxide tagged with C^{14} showed that the specific radioactivity of the newly formed carbon dioxide is intermediate between the specific radioactivities of ethylene and ethylene oxide at the instant of formation of CO_2 [34].

Additional experiments showed the absence of any appreciable exchange of C^{14} between C_2H_4O, or between either of these and CO_2. This shows conclusively that there are two simultaneous processes for the formation of carbon dioxide, by way of ethylene oxide and avoiding it. Twigg [33], whose findings concerning the sources of CO_2 formation are similar to ours, postulated the detailed reaction Scheme (11a) to explain the detailed kinetics of the reactions and the results of experiments on stepwise oxidation in a layer. The intermediate products in this scheme are acetaldehyde and formaldehyde, and there are two primary (5, 5' and 1,3,4) and three secondary (1,6; 1,7,8 and 1,3,9,8) directions of the process



(11a).

Our experiments with tagged ethylene oxide exclude the possibility of Process 2; experiments with tagged formaldehyde show that any appreciable development of Processes 5 and 5' is impossible; experiments with tagged acetaldehyde exclude routes 1,3,4; 1,7,8 and 1,3,9,8. Therefore, while the idea of two sources of CO_2 was confirmed, the Twigg scheme had to be radically revised [35]. Thus, none of the stable organic oxygen-containing compounds postulated by various authors as intermediates in the oxidation of ethylene to ethylene oxide and thence to carbon dioxide (and also in the oxidation of ethylene without involving ethylene oxide) can in reality play any significant part in these processes in presence of silver catalysts. The views on the nature of the primary processes leading to the formation of adsorbed ethylene oxide also proved erroneous [35]. Similar investigations were also made on the catalytic oxidation of ethylene and propylene over vanadium oxides. In these cases the composition of the products is entirely different. Practically no oxides of ethylene or propylene are formed, but carbon monoxide is found; aldehydes and acids predominate among the liquid products [36]. Each of these substances, tagged with C^{14}, was introduced into the reacting mixture, and it was found that none of them can be the main source of carbon dioxide, and that there is not even the simplest two-step chain of stable intermediate oxidation products for any of the substances in the catalytic process [37]. This changes our views radically not only on the oxidation of hydrocarbons, but also on the oxidation of some types of oxygen-containing organic compounds. Instead of a "staircase" of stable products of consecutive oxidation, it is necessary to assume a number of parallel sequences of oxidation reactions proceeding by way of labile substances of the unstable peroxide and radical type. Each of the stable oxidation products is formed to some extent independently, and can in its turn be completely oxidized by way of intermediate labile products. Such a scheme, without details of the probable composition of the intermediate labile compounds Y_1, Y_2, etc., is shown below for C_2H_4 [Scheme (11b)]. All Y_i are probably charged.

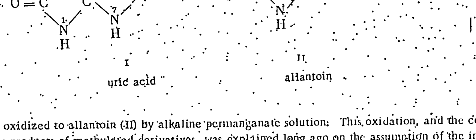


(11b)

The intermediate labile forms leading to the formation of different stable products may coincide, but none of the stable products of incomplete oxidation, C_2H_4O, CH_2O, CH_3OH, CH_3CHO, and $HCOOH$, passes to any practical extent into any of the others under oxidation conditions. According to kinetic data it is probable that the intermediate labile substances which take part in this process, in addition to others not conclusively determined, are O_2^- chemisorp, O^- chemisorp, and $C_2H_4O_2^-$ chemisorp.

Similar studies of homogeneous oxidation were performed by M. B. Neiman and his associates, who demonstrated the independent formation of CO and CO_2, and the unsuitability of CH_3CHO as the main intermediate product in the oxidation of butylene. M. B. Neiman et al. [38] made an interesting attempt to establish the point of oxygen attack in homogeneous oxidation with the aid of propylene molecules tagged with C^{14} in the central atoms, and acetaldehyde molecules tagged with C^{14} in different groups.

The participation of intermediate stable oxidation products in the process is not refuted in all cases by experiments with tagged molecules. An example is provided by the study of the mechanism of the oxidation of uric acid tagged in the nitrogen.



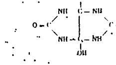
I

uric acid

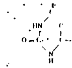
II

allantoin

Uric acid (I) is oxidized to allantoin (II) by alkaline permanganate solution. This oxidation, and the composition of the oxidation products of methylated derivatives, was explained long ago on the assumption of the intermediate formation of a hydroxy-carboxylic acid (III) with a symmetrical eight-membered heterocyclic ring containing nitrogen, intersected by a diagonal bond between two carbon atoms in the para-position [39]. The chemical structure of this intermediate compound is shown below:



III



IV

Attempts have been made to isolate this compound directly [40] and in the form of the silver salt [41], but the results were not wholly conclusive. To verify this hypothesis, Cavalieri and Brown [42] studied the distribution of N^{15} in allantoin formed by oxidation of uric acid tagged in atoms 1 and 3 of the six-membered ring. The synthesis of this acid was developed previously by these authors jointly with Blair [43]. The isotopic composition of nitrogen was the same in the ring and in the urea radical side chain [49]. This is in good agreement with the hypothesis of the intermediate formation of (III), in which the cleavage of the left hand and right halves of the eight-membered ring, which are completely identical, should be equally probable. Therefore, although only one of the two minor rings contains excess N^{15}, the oxidation products, to the accuracy of small isotopic corrections, should have the N isotope equally distributed among all the positions. This conclusion is probably correct, but for conclusive proof there should also have been experiments with specially introduced tagged molecules of (III), as it is still necessary to prove that the compound (III) is an intermediate and not a side product; also, the possibility is not excluded of oxidation with intermediate formation of other, more labile forms, such as symmetrical cyclic radicals or ions.

The same authors' experiments on the oxidation of tagged uric acid by nitric acid and chlorine showed that the alloxan (IV) formed contains all the tagged nitrogen from the original molecule, and therefore the alloxan ring contains the 1,3 nitrogen atoms and not the 7,9 atoms of the original (I) molecule. It is clear that in this case the intermediate formation of forms of type (III) is improbable. A similar conclusion had already been reached by others on the basis of a detailed study of the oxidation products.

The above investigation is one of many isotope studies dealing with determinations of the participation of different parts of an oxidized organic molecule in the formation of definite products. The same group of studies includes the investigation made by Fries and Calvin [44] of the permanganate oxidation of propylene; they found that the acetic acid, which is one of the reaction products, does not contain any of the methylene carbon, which is completely converted into CO_2

$$CH_2{=}CH{-}CH_3 — CH_3COOH + CO_2. \tag{12}$$

C^{14} was used in this work. In earlier studies, molecules tagged with short-lived C^{11} were used to study the oxidation, in solutions, of various carboxylic acids: propionic, α- and β-hydroxypropionic, fumaric, malic, and others, by powerful oxidizing agents. By variations of the oxidizing agent, solution pH, and other conditions, it is possible to vary within fairly wide limits the relative participation of carboxyl carbon and radical carbon [illegible] in the formation of oxalic acid and carbon dioxide from propionic acid, i. e., the ratio between the Reactions (13a) and (13b):

$$\overset{\beta}{C}H_3 - \overset{\alpha}{C}H_2 - \overset{*}{C}OOH \rightarrow \overset{\beta}{C}O_2 + HOO\overset{\alpha}{C} - \overset{*}{C}OOH, \tag{13a}$$

and

$$\overset{\beta}{C}H_3 - \overset{\alpha}{C}H_2 - \overset{*}{C}OOH \rightarrow HOO\overset{\beta}{C} - \overset{\alpha}{C}OOH + \overset{*}{C}O_2. \tag{13b}$$

When fumaric acid tagged with radioactive C^{11} in the carboxyl is oxidized by permanganate in an acid medium, all the radioactivity passes into the carbon dioxide; formic acid, which is the product of far-reaching oxidation, is formed entirely from the middle methine [46] carbon atoms

$$HOO\overset{*}{C}{-}CH{=}CH{-}\overset{*}{C}OOH$$

fumaric acid

without any appreciable participation of the carbon from the end carboxyl groups.

Thus, the genetic relationships between stable molecules in the oxidation of organic compounds have been intensively studied in two directions: 1) to distinguish between intermediate and side products and to determine the role of various products of incomplete oxidation in the process, and 2) to determine the nature of participation of different parts of the molecule in the process.

Less typical for the oxidation of organic compounds is a third direction: the determination of the original compound from which a particular end product is formed. An example of an investigation in which such a problem was solved is provided by the work of Taube and Dodgen [47], who studied a group of oxidation-reduction reactions of chlorine oxyacids with the aid of short-lived Cl^{38}.

It was shown in this investigation that in the reaction

$$HClO + ClO_2^- = ClO_3^- + Cl^- + H^+ \tag{14a}$$

the chlorate anion (ClO_3^-) is formed practically entirely from ClO_2^-, and chlorine from HClO does not enter it. In the reaction

$$4H^+ + 2Cl^- + 2ClO_3^- = Cl_2 + 2ClO_2 + 2H_2O \tag{14b}$$

practically all the chlorine dioxide is formed from the chlorate ion, and the molecular chlorine from the chloride ion. A curious result was obtained for the reaction represented by the stoichiometric equation

$$5HClO_2 = 4ClO_2 + Cl^- + H^+ + 2H_2O. \tag{14c}$$

catalyzed by Cl^- ions.

The tagged Cl^- ions practically do not pass into ClO_2, which excludes mechanisms with intermediate transfer of oxygen to the chloride ion. This is a particular instance of the use of tagged molecules to determine the nature of the participation of a catalyst in a reaction (see also §7 of this chapter).

These three directions do not exhaust the problems solved by analysis of the stage mechanisms of chemical reactions with the aid of tagged molecules. In particular, we have not considered the question of the nature of the intermediate labile forms, which are particularly important in oxidation in view of the prevalence of radical and chain mechanisms in reactions of this class. This direction, and the question of determination of the nature of the rate-controlling stage are discussed in §5 and 6.

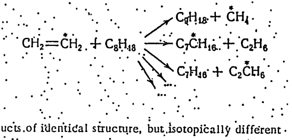
b) Determination of genetic relationships and verification of the mechanisms in other types of reactions

In the previous section the example of oxidation reactions was used to illustrate the main directions of the use of stable tagged molecules for determining the genetic relationships of the reactants.

Isotopic investigations of the genetic and structural relationships of reactants have also been used to a great extent in relation to other types of reactions. In this connection we may mention the Favorsky, Wagner, Beckmann, Claisen, and keto–enol rearrangements; the Menshutkin, Curtius, Arbuzov, Willgerodt, and other reactions, various types of aldehyde dismutation; transamination; nitration; isomerization of unsaturated and saturated hydrocarbons; catalytic cracking; syntheses based on carbon monoxide and hydrogen, etc. A systematic review of the enormous amount of material on the use of stable tagged molecules for investigations of chemical reaction mechanisms could form the contents of a separate extensive monograph, and therefore we shall consider only one additional example which extends the range of applications considered.

In thermal and catalytic cracking of hydrocarbons complex mixtures of saturated and unsaturated products, capable of entering side reactions, are formed. It is very difficult to determine the role of each by the ordinary methods, as the same substance may be formed in the main process or in a side reaction in which the reaction products react with the original hydrocarbon and with each other. Studies with the aid of carbon-tagged molecules are valuable for elucidating the actual, very complex relationships.

This was done in our laboratory for the catalytic cracking reaction in presence of aluminosilicate catalysts. The secondary reactions in the cracking of normal and iso-paraffins and cyclanes were studied by the distribution of C^{14}, introduced in individual tagged compounds (methane, ethane, ethylene, propylene, etc.) between the individual cracking products [48-50]. Some interesting relationships were found. Thus, in the homologous series of paraffins and olefins the reactivity increases systematically with molecular weight. Methane is particularly inert, not entering isotopic exchange either with paraffins or with olefins. In cracking, its radiocarbon is practically not found either in the nearest or in heavier paraffins, and does not enter the olefins, methane also practically takes no part in the formation of the coke formed on the catalyst. The other hydrocarbons undergo various reactions, among which the destructive alkylation which was first postulated by Maslyansky and Berlin for aromatic hydrocarbons [51] is predominant. This reaction, shown in Scheme (15) for octane and propylene, can lead to various products



$$CH_2{=}\overset{*}{C}H_2 + C_8H_{18} \rightarrow \begin{cases} C_9H_{18} + \overset{*}{C}H_4 \\ C_7\overset{*}{C}H_{16} + C_2H_6 \\ C_7H_{16} + C_2\overset{*}{C}H_6 \\ \ldots \end{cases} \tag{15}$$

including the following products of identical structure, but isotopically different

$$CH_2{=}\overset{*}{C}H_2 + C_8H_{18} \rightarrow CH_2{=}CH_2 + C_7\overset{*}{C}H_{18}. \tag{15a}$$

Olefin polymerization also occurs, and coke is deposited on the catalyst; this is particularly intensive for olefins. The difference in the reactivities of olefins and paraffins in this respect diminshes with increasing molecular weight. By the use of C^{14} it proved possible to follow the hydrogenation of olefins and dehydrogenation of paraffins, with clear differentiation between the processes, in the complex cracking conditions. In particular, in the case of olefins it is possible to discriminate between the redistribution of hydrogen among hydrocarbons of the same molecular weight, leading only to isotopic exchange,

$$\overset{*}{C}H_2{=}CH{-}CH_3 + CH_3{-}CH_2{-}CH_3 \rightleftharpoons \overset{*}{C}H_3{-}CH_2{-}CH_3 + CH_2{=}CH_2{-}CH_3, \tag{16}$$

hydrogenation by the coke,

$$\underset{\text{coke}}{C_mH_n} + \overset{*}{C}H_2{=}CH{-}CH_3 \rightarrow \underset{\text{coke}}{C_mH_{n-2}} + \overset{*}{C}H_3{-}CH_2{-}CH_3 \tag{17}$$

and hydrogenation by paraffins with a different number of carbon atoms

$$\overset{*}{C}H_2{=}CH{-}CH_3 + C_4H_{10} \rightleftharpoons \overset{*}{C}H_3{-}CH_2{-}CH_3 + C_4H_8. \tag{18}$$

It was also found that in the cracking of methylcyclohexane, reversible isomerization occurs, leading to intramolecular isotopic exchange [50]

$$C_6H_{11}\overset{*}{C}H_3 \rightarrow C_5\overset{*}{C}H_{11}CH_3, \tag{19}$$

the mechanism of which was discussed in § 2, Chapter I. These researches convincingly demonstrate the importance of isotopic verification of the chemical behavior of each of the products in a complex reaction. As a rule, whenever this was done, new and previously unknown stages and formerly undetected side reactions have been discovered. The introduction of tagged molecules into a reacting system in order to establish the genetic relationships of the substances, and groups and atoms constituting the molecules, is likely to become in the near future the principal method for the study of hidden and secondary side processes in complex chemical reactions, and the irreplaceable means for establishing the stage mechanism. However, for this it is important to study the behavior of all the stable substances formed in a given reaction.

Numerous examples of the successful application of tagged stable molecules to investigations of reaction mechanisms are contained in special monographs and reviews dealing with the use of isotopes in chemistry, biology, and technology [52-56], and in recent monographs on general problems of kinetics, biochemistry, etc., in which the results of isotope studies are taken into account [10, 57]. However, this is only the beginning. Until all the main reaction types and all the most characteristic and interesting chemical reaction stages have been subjected to detailed verification with the use of isotopes, if possible not only of one but of all the elements present in the reactants, there can be no certainty that the schemes representing their mechanisms are correct or complete. This is one of the basic tasks of modern theoretical chemistry, for the fulfillment of which tagged molecules and isotopic investigation methods must be adopted for everyday use in laboratories in which chemical processes in any field are studied.

Tagged molecules have produced many valuable results in studies of reactions of small molecules in the gas phase and in dilute solutions. It is, however, no accident that isotope studies of reaction stages are predominant for reactions of large molecules in complex conditions, as in biology. A valuable feature of tagged atoms and molecules, especially those containing radioactive isotopes, is the possibility of studying the genetic and structural relationships of individual substances in conditions of any degree of complexity in multicomponent systems, in large industrial equipment, in the soil, in biological synthesis by microorganisms, in photosynthesis in plants, in metabolism in higher animal organisms, etc. Examples are provided by the proof, by means of C^{14}, of the participation of carboxylic and methyl carbon of acetic acid in the formation of different parts of the cholesterol [58] and ergosterol [59] molecules, the work of Soviet investigators on the nitrogen nutrition and metabolism of plants with the use of N^{15} [60], and on carbon metabolism in the animal organism with the use of C^{14} [61].

When such genetic investigations are applied to macroscopic material, a new and interesting possibility arises of establishing the topography of the process; i. e., determining the origin, route, and destination of translocation of substances and individual groups, and their location in the final product. This possibility is extensively used for studying processes in industrial units [62], in agricultural chemistry, biology, and medicine [63]. A striking example of the effectiveness of this method is provided by the use of C^{14} to establish the existence of dark photochemical assimilation of atmospheric carbon dioxide by plants [64]; the absorption of carbon dioxide by plant roots from the soil [65], and the final refutation of the theory that aldehydes, and in particular formaldehyde, are formed from water and carbon dioxide

$$CO_2 + H_2O \rightarrow H_2CO + O_2 \tag{20}$$

as the primary photosynthesis process [56, 66].

§ 4. M. B. Neiman's Kinetic Isotope Method

The use of isotopes as tracer atoms for establishing the genetic relationships between stable substances participating in complex chemical reactions, and for studying reaction mechanisms, has raised a number of new kinetic problems. Work on these problems is in its early stages, and detailed kinetic analysis is being avoided in most individual investigations. A promising method for the simultaneous solution of equations for the kinetics of a chemical process and the variation of the isotopic composition has been proposed by M. B. Neiman and his associates [67]; it has been termed by them, in an unsubstantiated generalization, "the kinetic isotope method" and "the kinetic method of the use of tagged atoms for studying the mechanisms of complex chemical and biochemical processes."

The object under consideration in this method is the common, but by no means universal type of chemical processes which occur with the formation of intermediate substances which can be isolated individually. In addition to such reactions, complex processes are very common in which the intermediate products are only highly active labile substances – free atoms, radicals, carbonium ions, excited molecules, and other substances which cannot be isolated or kept. The discussion presented below is not applicable to such processes, nor to systems of parallel simple reactions and chemical reactions complicated by exchange of the isotopes introduced as tracers. Moreover, in the use of this method it is necessary to know in advance what the intermediate substance is, and to exclude its reverse reactions.

In his latest and most complete paper [68] M. B. Neiman considers the type of process schematically represented as

$$\begin{tikzcd}[column sep=small, row sep=small]
\cdots \arrow[r] & A_1 \arrow[dr] & & B_1 \arrow[r] & \cdots \\
& & X \arrow[ur] \arrow[dr] & & \\
\cdots \arrow[r] & A_2 \arrow[ur] & & B_2 \arrow[r] & \cdots
\end{tikzcd}$$

One substance A_1, or several substances A_1, A_2, etc., react chemically, forming an intermediate substance X. In its turn, X is consumed in one or several parallel reactions, forming the products B_1, B_2, etc. All the individual processes are assumed to be irreversible. In these conditions accumulation of the intermediate product X is represented by the equation

$$\frac{dx}{dt} = \sum k_i[A]_i - \sum k'_j[X]. \tag{21}$$

In reality, each k_i and k_j may contain, in concealed form, variable concentrations of other substances B, C, D, etc., first order with respect to A and X is also by no means obligatory. The subsequent analysis is applied to a particular case, when $\Sigma k'_j[X]$ can be substituted by kx. On the other hand, no special restrictions are placed on the sum $\Sigma k_i [A]_i$, which represents the rate w of formation of the intermediate product.

In these conditions,

$$\frac{dx}{dt} = w - kx; \tag{22}$$

Variation of the content of tagged $\overset{*}{X}$ molecules is then considered. If their concentration is denoted by $\overset{*}{x}$ and the specific content of the tagged molecules is denoted by α

$$\alpha = \frac{\overset{*}{x}}{x} \tag{22a*}$$

and the kinetic isotope effect is neglected, the rate of change of $\overset{*}{x}$ can be written, analogously to (22), as

$$\frac{d\overset{*}{x}}{dt} = \overset{*}{w} - k\overset{*}{x}; \tag{23}$$

The different molecules of the original substances which give rise to X are assumed to have a certain equal content of the tagging isotope $\overset{*}{X}$; $\beta \equiv \rho$.

$$\beta = \frac{[\overset{*}{A}_1]}{[A_1]} = \cdots \frac{[\overset{*}{A}_i]}{[A_i]}, \text{ etc.} \tag{23a}$$

With these assumptions

$$\frac{d\overset{*}{x}}{dt} = \beta w - k\alpha x, \tag{24}$$

and, after simple transformation,

$$\frac{d\alpha}{dt} = \frac{w(\beta - \alpha)}{x}. \tag{25}$$

For the special case when $\beta = 0$

$$\left.\begin{aligned} &\frac{d\alpha}{dt} = -\frac{\alpha w}{x}, \\ \text{or}\quad &\frac{d\ln\alpha}{dt} = -\frac{w}{x}. \end{aligned}\right\} \tag{26}$$

---

* In our earlier notation this is $\rho_{\overset{*}{X}} = \frac{[\overset{*}{X}]}{[X]}$.

Then, by finding the isotopic composition and content of X at various time instants after addition of $\overset{*}{X}$, an attempt is made to determine the experimental variation of x and α with time

$$\left.\begin{aligned} &\text{a)}\quad x = f(t); \\ &\text{b)}\quad \alpha = \varphi(t), \end{aligned}\right\} \tag{27}$$

and, by differentiation with respect to t, the derivatives of these functions

$$\left.\begin{aligned} &\text{a)}\quad \frac{dx}{dt} = f'(t); \\ &\text{b)}\quad \frac{d\alpha}{dt} = \varphi'(t), \end{aligned}\right\} \tag{28}$$

These four functions are used to write expressions for w and kx

$$w = F(t) = -\frac{f(t)\varphi'(t)}{\varphi(t)} \tag{29}$$

$$kx = -\frac{f(t)\varphi'(t)}{\varphi(t)} - f'(t). \tag{30*}$$

Division of (29) by x gives k. In view of the laborious nature of isotope analysis and the practical impossibility, in most cases, of obtaining reliable data for the exact determination of f and φ, the above method for determining w and k is, of course, very inaccurate. These critical comments are substantiated by the published results of an application of the method to homogeneous oxidation [69, 70]. In these investigations the authors used a kinetic method for determining the role of acetaldehyde in the cold flame region and reached conclusions which were in sharp contradication to the concepts based on the very careful work of V. Ya. Shtern and S. S. Polyak [71, 72]. However, it was later found that the method of introducing the tagged substances in the investigations [69] and [70] was incorrect, and this led to internal contradictions in the treatment of the data by the kinetic isotope method. A repetition of the same work in improved conditions resulted in agreement with the results of Shtern and Polyak [73]. At least two independent sources both of carbon monoxide and of carbon dioxide were found, through acetaldehyde and avoiding it. In this respect the findings of M. B. Neiman *et al.* concerning homogeneous noncatalytic oxidation are similar to our conclusions for the heterogeneous catalytic oxidation of olefins. It is not clear whether the conclusion drawn from the work with methane [74], in which all the carbon monoxide was formed from formaldehyde, is to be regarded as final.

Some small modifications were introduced into the calculation method in the last paper on the oxidation of methane. The expression for the formation rate of the intermediate product was put into the form

$$w_1 = -x\frac{d\ln\alpha}{dt}, \tag{31}$$

the expression for its rate of consumption was

$$w_2 = -x\frac{d\ln\alpha}{dt} - \frac{dx}{dt}, \tag{32}$$

and the following equation was used to calculate the formation rate of the final products (CO and CO_2)

$$w_{\text{final}} = \frac{1}{\alpha} \cdot \frac{dI}{dt}, \tag{33}$$

where I is the total radioactivity of carbon monoxide and dioxide; α is the specific radioactivity of acetaldehyde in all cases.

---

* Or, which is the same thing, $w = -f(t)\,d\ln\varphi(t)$; $kx = -f(t)\,d\ln\varphi(t) - f'(t)$.

§ 5. Detection of Intermediate Labile Forms and Verification of Chain Mechanisms

a) The significance of labile forms

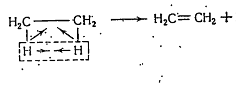
As was pointed out at the beginning of this chapter, one of the most general characteristics of chemical reactions is the determining participation of intermediate active forms. This is true for reactions induced by any forms of energy, in any phase and external conditions. The frequent occurrence of reactions in which the intermediate active forms are free or solvated ions, free atoms, and mono- or biradicals, has been firmly established. Electronically excited molecules play an important part in photochemistry. The position of vibrationally and rotationally excited molecules in chemical kinetics is less clear. Peculiar active forms, which evidently do not fit into the above types, participate in chemical reactions of solids and in reactions accelerated by them. The role of gaps in crystal lattices, deviations from stoichiometric relationships, and micro-admixtures in such processes is undoubted. They are associated with the formation of atoms and ions with unusual charges, which regulate the concentration of free electrons and electron holes in the lattice, and are the most active forms in heterogeneous processes. A considerable proportion of the active forms described by the common term of "active centers" in heterogeneous catalysis is probably to be ascribed to the same types of active particles and to proton excess and deficiency. In any processes involving the formation or disappearance of crystalline phases, surface and volume nuclei are added to these forms. Thus, more than ten types of active particles which take part in chemical processes are known with certainty, and there is no doubt that new, as yet unknown types will be discovered in the future. The lives of different forms differ under the same conditions. Thus, some types of active ions in solutions are thermodynamically stable and can therefore exist for indefinitely long periods. Thermodynamically unstable, labile forms are more typical and frequent. The typical lives of free atoms and radicals in gases are measured in hundreths and thousandths of a second. The lives of electronically and vibrationally excited molecules are still shorter. However, all these life periods considerably exceed the life periods typical for intermediate complexes, which are obligatory intermediate forms in the vast majority of processes, including processes involving the other active forms mentioned above. The lower limit of the life periods of intermediate complexes coincides with the duration of collisions in gases and of thermal vibrations in solids and liquids, i. e., 10^{-10}-10^{-12} seconds.

The detection of active forms characteristic of different types of processes, studies of the chemical characteristics and physicochemical properties of these forms, and as a result, the establishment of the basic laws of the chemistry of active forms, is one of the central problems of modern chemical kinetics. The success of researches into the reactivity of matter, and the deliberate utilization of active forms for bringing about new and controlling old processes, largely depend on the successful solution of this problem. This is especially important in relation to thermal and radiochemical chain reactions.

Numerous different methods are used in modern kinetic investigations for detection of active forms and measurement of their concentrations. Among the direct methods for the detection of active forms, optical spectroscopic methods occupy an honored position. In recent years these have been challenged by radiowave and microwave methods (in particular, paramagnetic resonance studies), magnetic methods play an important part, mass spectrometry is very promising for gases, and for solids and solutions electrical conductance determinations are successfully used. There are numerous indirect thermal, kinetic, and other methods for the investigation of active forms. Direct investigations of reactions of artificially produced active particles have great significance in studies of the reactivity of active forms and for verifying the mechanisms of their participation in chemical processes. Thus, the whole range of the best modern methods is used for studying active intermediate forms; however, the difficulties are such that reliable and conclusive results are accumulating only slowly. It may be said in general that the successful use of any particular special method is largely determined by its skillful use in conjunction with other methods, and by the available knowledge of the chemistry and kinetics of the reaction in question. This also applies fully to the large group of isotopic methods for the study of active forms.

b) Methods based on deuterium exchange

A group of promising methods for studying active forms is based on deuterium exchange investigations. In Chapters III and V an account was given of the characteristic deviations from the most probable distribution of molecules according to the degree of replacement of protium by deuterium, which arise when free atoms and radicals are present in a system. Chapter III contains a detailed examination of examples of the acceleration of hydrogen isotope exchange and of the increase of the number of atoms involved in the exchange, caused by tautomeric rearrangements, reversible dissociation, and other hidden processes which occur with the participation of active forms. The method of isotopic mixing, which is included in this group, developed recently for the detection of radical and chain processes in the pyrolysis of organic compounds, deserves special attention. This method was first proposed by Wall and Moore [75] in 1951, to verify the Rice-Herzfeld theory [76, 77] of the radical mechanism of hydrocarbon pyrolysis. It was later developed and improved by others, and its applicability has been extended. The basic idea of the method lies in the use of additional isotopic exchange of hydrogen, caused by hydrogen redistribution between radicals and saturated molecules, for the detection of radical chain reactions. In the ideal case, in a practically irreversible process, the only active form in a process following a molecular mechanism is an intermediate complex, and no genetic relationship exists between different specimens of the reacting molecules. The situation is different in radical chain processes, where each of the initially formed centers induces the formation of several (or many) others, and the intermediate active forms exist sufficiently long to exert an influence on isotopic exchange. This can be illustrated by the pyrolysis of ethane. At not very high temperatures dehydrogenation predominates; with a molecular mechanism this reduces to an intramolecular regrouping



(34)

In the pyrolysis of a mixture of C_2H_6 with C_2D_6 the products should contain only C_2H_4, C_2D_4, H_2, and D_2. Neither HD, nor ethylene or ethane of mixed isotopic composition should be formed. The dehydrogenation should be quite different according to the Rice-Herzfeld theory, in which primary dissociation of ethane into two methyl radicals is postulated:

$$\left.\begin{aligned} C_2H_6 &\rightarrow 2CH_3; \\ C_2D_6 &\rightarrow 2CD_3. \end{aligned}\right\} \tag{35}$$

By further reactions with ethane of the same and other isotopic compositions, these radicals can in principle give rise to a series of secondary processes:

$$\left.\begin{aligned} CH_3 + C_2H_6 &\rightarrow CH_4 + C_2H_5; \\ CH_3 + C_2D_6 &\rightarrow CH_3D + C_2D_5; \\ CD_3 + C_2D_6 &\rightarrow CD_4 + C_2D_5; \\ CD_3 + C_2H_6 &\rightarrow CD_3H + C_2H_5; \end{aligned}\right\} \tag{36}$$

$$\left.\begin{aligned} CD_3 + C_2H_6 &\rightarrow CD_3CH_3 + CH_3; \\ CH_3 + C_2D_6 &\rightarrow CH_3CD_3 + CD_3; \\ CD_3 + CH_3 + M &\rightarrow CD_3CH_3 \end{aligned}\right\} \tag{37}$$

etc. According to Rice and Herzfeld, Reaction (36), which leads to formation of ethyl radicals, ends the initiation of chain dehydrogenation. This is followed by a chain repetition of the Reactions (38)

$$\left.\begin{aligned} C_2H_5 &\rightarrow C_2H_4 + H; \\ C_2D_5 &\rightarrow C_2D_4 + D, \end{aligned}\right\} \tag{38}$$

and then

$$\left.\begin{aligned} H + C_2H_6 &\rightarrow C_2H_5 + H_2; \\ D + C_2D_6 &\rightarrow C_2D_5 + D_2; \\ H + C_2D_6 &\rightarrow C_2D_5 + HD; \\ D + C_2H_6 &\rightarrow C_2H_5 + DH. \end{aligned}\right\} \tag{39}$$

Consequently, in chain dehydrogenation of mixtures of ordinary and deuterated ethane, DH should be formed together with D_2 and H_2, while the side reactions (37), together with hydrogen exchange according to Voevodsky [78, 79], which was not taken into account by the American authors, may lead to formation of ethane, and radicals of mixed hydrogen isotope compositions. A characteristic result of the mechanism should be the formation of methane, which , in mixtures of C_2H_6 and C_2D_6, should contain CH_3D and CD_3H in corresponding proportions. Wall and Moore [75] found this to be the case, and they also showed that the addition of nitric oxide which, according to Hinshelwood et al., inhibits ethane pyrolysis and terminates the chain [80, 81], also strongly retards "isotopic mixing" in methane and ethane. Subsequent work revealed imperfections in the pioneering research of Wall and Moore, and the faults of the method in its original form were eliminated in later studies. In this context special mention must be made of the work of Rice and Varnerin [82] who showed the advantages of combining differences in isotopic composition with differences in chemical composition. To the decomposing substance, for example ethane, it is advantageous to add as an isotopic mixing tracer a substance which is capable of isotopic exchange with the radicals, but which is not itself decomposed in these conditions. In the case of ethane it proved to be the most convenient to use a deuterated C_2D_6 substrate mixed with methane free from deuterium. The chain nature of the pyrolysis was established with reasonable certainty in these conditions. In a later paper by the same authors [83] it is shown that the decomposition of completely deuterated molecules with tracers of a different chemical composition can be used for determination of differences in the rate constants and activation energies of reactions between $\dot{C}H_3$ and CD_3 radicals and various organic compounds. The numerical results obtained are in good agreement with the most reliable data obtained by other methods. The development of the isotopic mixing method cannot be considered complete; in particular, additional exchange between radicals according to Voevodsky [78, 79] must probably be taken into account, but there is no doubt that it is highly promising. Most of the investigations by this method have dealt with the homogeneous pyrolysis of ethane. The pyrolysis of n-butane [84], acetaldehyde, and acetone has also been studied. A critical review of the results obtained up to 1954 is contained in the second edition of Steacie's monograph [57].

The applications of the isotopic mixing method are not confined to the detection of free radicals and chain processes. Skillful use of this method gives valuable information on the reactivities of radicals. For example, Zemany and Burton [85] studied the mixing of hydrogen isotopes in methane formed by photolysis of mixtures of CH_3CHO and CD_3CDO and in acetaldehyde, and obtained interesting indications of the existence of methyl radical exchange by the reaction

$$\mathrm{CH_3 + CD_3CDO \rightarrow CH_3CDO + CD_3}. \tag{40}$$

Carrying out the same reaction pyrolytically, Wall and Moore [86] discovered an anomalously high CH_2D_2 content, indicating direct hydrogen exchange between radicals

$$\mathrm{CH_3 + CD_3 \rightarrow CH_2D + CD_2H}. \tag{41}$$

These findings cannot be regarded as conclusive, but there are no obstacles in principle to the quantitative determination of the role of these two interesting processes by this method. More conclusive results were obtained by Blacet and Brinton [87] by the isotopic mixing method in the photolysis of the same system. It was found that in their reaction with acetaldehyde the methyl radicals detach hydrogen from the acyl group according to Equation (42), while the alkyl hydrogen is almost untouched

$$\left.\begin{array}{l}\mathrm{\dot{C}H_3 + CH_3CHO \rightarrow CH_4 + CH_3\dot{C}O;}\\ \mathrm{\dot{C}H_3 + CH_3CDO \rightarrow CH_3D + CH_3\dot{C}O.}\end{array}\right\} \tag{42}$$

Isotopic mixing in the products practically ceases on addition of iodine which, according to some authors [88, 89], reacts with methyl, terminating the chain. In these experiments deuterium acted as a tracer introduced into a definite group (CHO) of a stable molecule. The success of Blacet and Brinton's work largely depended on the application of the isotopic mixing method to molecules tagged in a definite position. The same method was applied by Wijnen and Steacie [90, 91] in a study of the chemical properties of ethyl radicals. Diethyl ketone deuterated in the secondary carbon, $(CH_3CD_2)_2CO$, was subjected to photolysis. It is known from ordinary photochemical data that a side reaction of hydrogen redistribution between two primary radicals occurs

$$\mathrm{2C_2H_5 \rightarrow C_2H_6 + C_2H_4}. \tag{43}$$

Investigation of the isotopic composition of the ethane and ethylene formed by photolysis showed that in the reaction between the two radicals the redistribution occurs only between methyl and methylene hydrogens of two molecules, and exchange between analogous groups of two radicals may be neglected; i. e., the following transition occurs:

$$\mathrm{CH_3C}\overset{\curvearrowleft}{\mathrm{D_2 + H}}\mathrm{CH_2CD} \tag{44}$$

while the following transition is practically absent:

$$\mathrm{CH_3\dot{C}D}\overset{\curvearrowleft}{\mathrm{H + \dot{D}}}\mathrm{CDCH_3 \rightleftarrows CH_3CD_2 + CH_3CHD} \tag{45}$$

It also follows from the same results that rapid isomerization of ethyl radicals does not take place

$$\mathrm{CH_3\dot{C}D_2 \rightleftarrows CH_2\dot{C}D_2H \rightleftarrows CH\dot{D}CH_2D}, \text{ etc.} \tag{46}$$

In conjunction with other methods, isotopic mixing studies can be used for comparing the rates, activation energies, and k_{∞} of various radical reactions, for determining the activation energy of radical formation, which is also the kinetic energy for the rupture of definite bonds, etc.

The results obtained are most valuable if, by the conditions for the decomposition of the original molecules, deuterium-tagged free radicals are formed in the reaction medium, and the isotopic mixing method serves only to determine the predominant direction of their reactions. This technique is important in principle, and it has an important future.

c) Tagged atoms and radicals

When a definite active form can be produced artificially in definite concentrations, its introduction in tagged form into a system makes it possible, in principle, to study the nature of the participation of this form in the given process. For this, in some cases, the corresponding active form of unusual isotopic composition is prepared outside the reaction space and then introduced into it; in other cases it may be formed directly in the reaction space. The main task is not the study of the influence of a particular active form on the aggregate process (which does not require tagged atoms and molecules), but the fate of the tagged atoms and their distribution between the various reaction products, which indicate the genetic relationships between the active forms and the reaction products. Considerable difficulties are created in this approach by the instability of the active forms, their increased tendency to isotopic exchange, and the superposition of side reactions which are difficult to take into account. It is usually simpler to introduce into the system, not the active forms themselves, but ordinary molecules which produce them in the reaction conditions. For example, the pyrolysis of organic mercury compounds and azo compounds in a reaction space with biacetyl may act as a source of aliphatic radicals; organic peroxides may decompose to yield peroxide radicals, etc. In other cases, as we have seen, it is possible to use selective photochemical decomposition of stable substances which decompose into radicals under the influence of definite wavelengths.

Of the investigations with direct use of tagged atoms and radicals, we shall consider studies of the hydrogenation of ethylene. It was shown as early as the 1920's that acetylene induced rapid recombination of atomic hydrogen and that, in contrast to ethylene, it is not itself hydrogenated appreciably in the process. Spectroscopic analysis of the luminescence which accompanies this peculiar catalytic exchange indicated the formation of strongly unsaturated $\cdot\dot{C}H$ and $\dot{C}_2$ radicals in the reaction. This suggests extensive decomposition and dehydrogenation of parts of the molecules, perhaps according to the scheme:

$$\left.\begin{array}{l}\mathrm{C_2H_2 \rightarrow CH + CH,}\\ \mathrm{C_2H_2 \rightarrow C_2 + H_2}\end{array}\right\} \tag{47}$$

with the probability of closed cycles of radical reactions, completed by reformation of acetylene [92, 93]. This was confirmed by Geib and Steacie [94], who studied the reaction of ordinary acetylene with atomic deuterium. They showed that, despite the absence of any appreciable hydrogenation of acetylene, the latter completely exchanges its hydrogen with the deuterium while in the reaction tube. This indicates a stage mechanism

$$\left.\begin{array}{l} C_2H_2 + D \rightarrow C_2H + HD, \\ C_2H + D \rightarrow C_2HD, \text{ etc.} \end{array}\right\} \quad (48)$$

or

$$\left.\begin{array}{l} C_2H_2 + D \rightarrow C_2H_2D, \\ C_2H_2D + D \rightarrow C_2HD + HD. \end{array}\right\} \quad (49)$$

A second example of the use of tagged atoms and radicals introduced into the reaction medium from outside are the experiments of V. V. Voevodsky et al. [78, 95] with aliphatic radicals, described in Chapter III. These radicals were obtained by the reaction of free hydrogen atoms with olefins and then mixed with the substance under investigation. In this way the authors were able to demonstrate increased ease of hydrogen exchange without alteration of radical structure, which may be the prototype of certain elementary free radical reactions. The results would have been more conclusive and interesting if a mass-spectroscopic study of the exchange products had been made, and if completely deuterated radicals, which are easily prepared by the same method, had been used.

Applications of hydrogen isotopes to studies of intermediate forms are not confined to free atoms and simple radicals in the gas phase. Chapter III described the results of a verification, by means of mass spectrometry of the molecules, of the carbonium mechanism for exchange and isomerization in the liquid phase. In recent years numerous similar investigations of various reactions in solutions have been published, the actual methods of using hydrogen isotopes for this purpose being extremely varied.

Possible in principle, but not yet achieved, is the development of similar methods for the study of active intermediate forms by the isotopic mixing of other elements, such as halogen isotopes in the reactions of organic halides containing several halogen atoms in the molecule. Studies of complex reaction mechanisms are also by no means restricted to particles tagged with hydrogen.

Radicals containing tagged carbon are successfully used for complex organic reactions. This method has been especially widely developed for studies of polymerization processes. By the introduction of carbon-tagged molecules such as $(CH_3)_2(CN)CN{=}NC(CN)(CH_3)_2$, which produce radicals, as initiators in the polymerization of vinyl compounds, it proved possible to determine the proportion of the radicals usefully utilized in initiation of the chain process. In the case of methyl acrylate this fraction was close to 0.5. Subsequently, tagged radicals were also used to determine the nature of the side processes in which the other half of the radicals are consumed.

The use of molecules tagged with C^{14} has provided valuable information on the mechanism of inhibitor action, copolymerization, the chemical nature of chain termination, macromolecular branching in polymerization, etc.

Important details have rapidly been added to the polymerization scheme of divinyl derivatives by means of isotope methods, and the theory of this important group of radical chain processes has become more definite and more quantitative. It is not possible to consider all the numerous individual publications here, but reference must be made to the interesting review by Bevington and Melville [96], to whom most of the credit is due for the successful use of radiocarbon in investigations of diene polymerization from various aspects.

A discussion of the use of tagged atoms and molecules in kinetic investigations naturally leads to a consideration of their use for studying chain reactions. Mention must be made in this connection of the as yet unrealized possibility of studying of the kinetics of reversible chain reactions at established equilibrium by means of isotopic exchange; this would help to explain how the peculiar kinetic relationships observed for chain reactions far from equilibrium are compatible with the restrictions applied by chemical thermodynamics on the chemical process at equilibrium. It must be pointed out that the great possibilities inherent in the use of isotopes for the study of the rates of balanced reactions and reaction steps are still being used quite insufficiently for the solution of other kinetic problems.

§ 6. Determination of the Structure of Intermediate Complexes and of the Nature of the Bonds Broken and Formed at the Rate-Determining Stage

It can be regarded as definitely established that each elementary chemical step which occurs on collision of particles or by regrouping of atoms and bonds within a molecule is effected with the intermediate formation of a strictly definite endothermic transition complex. This is equally true for the reactions of stable neutral molecules, free atoms, radicals, and ions, in gaseous, liquid, and solid phases.

In complex homogeneous and heterogeneous chemical reactions each individual step has its own intermediate complex. The composition of this complex determines the order of the elementary process, the energy of formation of the complex determines the activation energy of the process, the nature of the internal motion of the complex (through the entropy of formation) determines the value of the pre-exponential factor in the rate constant for the process. Thus, the properties of the intermediate complexes determine the manner in which the rates of simple chemical processes depend on the concentrations (activities) of the reactants, the absolute values of the rate constants, and their variations with the temperature.

Since, in principle, the course of any process, no matter how complex, is determined by the nature and the rates of its component simple processes, the properties of the intermediate complexes in individual stages of consecutive reactions play a prominent role in the theory of complex reactions also. They primarily determine the relationship between the various directions of a process and the nature of the intermediate and side products. Therefore the general level of chemical kinetics depends considerably on the level of our knowledge of intermediate complexes. Until recently the only properties of intermediate complexes which could be determined experimentally were the energy of their formation and their chemical composition. The former were found from the temperature rate coefficients which, with the appropriate corrections, give the true activation energies, i. e., according to the statistical theory, the true energies of formation of the intermediate complexes. Unfortunately, these values cannot always be determined for systems far from ideality. What molecules, and in what numbers, are associated in the intermediate complex could in principle be found from the reaction order, after application of corrections for deviations of the system from ideality. However, no direct methods for determination of the structure, energetics, and nature of the internal motions in the intermediate complex were available. Because of the low absolute concentrations of the intermediate complexes, the usual optical and electrical methods are inapplicable for this purpose; microwave methods are more promising, but so far they have not been used for this. The only sources of additional information until recently were investigations of small changes in rate constants caused by external conditions – pressure, electric fields, etc.

The position was made still more unsatisfactory by the fact that the gap in the direct experimental data could not be filled by calculation, as quantum-mechanical calculations of the activation barriers, which form an essential part of calculations of absolute reaction rates, are unreliable and have only very low accuracy. In this situation especially great importance attaches to the possibility, indicated in Chapter IV, of using the values of kinetic isotope effects for determining such important structural characteristics of intermediate complexes as the nature of the chemical bonds formed or broken at the stage which determines the rate of the process in the given conditions. This possibility follows from the statistical theory of kinetic isotope effects, which shows that the terms which prevent exact absolute calculation of the equilibrium of the intermediate complex vanish from the final expressions by cancellation in the corresponding fractions.

Chapter IV contains numerous examples of the application of this method to the investigation of the mechanisms of different types of reactions. For example, it was shown for acid–base catalysis (see §12, Chapter IV) that the relationship $k_{Tobs} > k_{Dobs} > k_{Hobs}$, often found for acid catalysis in aqueous solutions, is possible only if the rate of the process is determined by the decomposition of the intermediate complex, the decomposition of ethyl bromide was used to illustrate the possibility of choosing between radical and molecular reaction mechanisms, etc. In this connection we may mention the interesting results obtained by Kaplan [97], who demonstrated, by determination of the tritium isotope effect in the oxidation of ethanol by bromine, the transfer of H^- and correspondingly of T^- ions at the the determining step. This conclusion is in good agreement with the isotopic data obtained by Melander for other reactions of ethanol and methanol [98].

Chapter IV also gives the results of experimental tests of the quantitative derivations from the theory for intramolecular and intermolecular isotope effects. In some cases the results of these tests are quite favorable for the theory, which confirms its reliability for the initial postulates. However, when no such agreement is found, new interesting problems are posed by the search for the causes of the discrepancies. For example, the systematic deviation of the calculated results from experimental data for the isotope effects in the reaction between molecular hydrogen and atomic chlorine was noted in Chapter IV.

The possible causes of this deviation were subjected to detailed analysis in two papers by Bigeleisen and Wolfsberg [99]. In the first of these (1953) the authors cast doubt on the validity of the generally accepted hypothesis concerning the linear arrangement of a chlorine atom and two atoms of the hydrogen molecule in the intermediate complex which determines the rate of the reaction $Cl + H_2 \rightarrow HCl + H$, and obtained better agreement with a triangular symmetrical model for the intermediate complex. However, a subsequent more detailed investigation, with careful determinations of all the vibrational frequencies of the intermediate complex and of the rotational and tunnel corrections showed that the experimental data are compatible both with a triangular and a linear complex, with a definite ratio of the rate constants for the two reaction directions in HD and HT molecules. The final choice between these two models is not yet possible, but the 1955 paper shows what determinations are required for this choice to be made [99].

It is probable that a revision of the models is also needed in the theory of the intramolecular isotope effect in the decarboxylation of malonic acid, for which, according to the latest very careful determinations of Yankwich et al. [100], α 1.0292 ± 0.0007 for decomposition in melts and 1.0284 ± 0.0012 for decomposition in quinoline solution (both values at 140°C). The theoretical value of α according to Bigeleisen is considerably less, 1.0198.

We may also mention the important improvements introduced into the theory of the calculation of activation energies for the reactions of methyl radicals with hydrogen, based on experimental values of the isotope effects [101]. Thus, precise determinations of kinetic isotope corrections provide a powerful method for studying the nature of intermediate complexes and for developing their theory. By successive variation of the nature of the rate-determining stage by changes in the experimental conditions, it may prove possible to determine the nature of several or even of all the intermediate complexes in a multistage reaction.

Systematic determinations of small deviations between theoretical and experimental data offer interesting possibilities, as they conceal the possibility of a transition from the ideal model of the intermediate complex, in which only several directly participating stages are taken into account, to a real model, which takes into account the mutual influence of bonds in the intermediate complex, its detailed structure, energy relationships, and the nature of the participation of solvents and catalysts.

An instructive example of the useful results obtainable in this way is provided by the latest work of Stranks [102] on the C^{14} isotope effect in the isotopic exchange of complex carbonate ions of trivalent cobalt with carbonate ions, and the isotopic exchange of carbon monoxide tagged with C^{14}, with phosgene [103], and the work of Lewis and Boozer on the isotope effect in the chemical reactions of the carbonium ion [104].

Further accumulation of accurate experimental data should reveal possibilities of generalizations which permit the nature of intermediate complexes to be predicted from the composition and chemical structure of the reactants. The intermediate complexes will lose their mysterious character, and their properties will become as well known as the properties of other types of active molecules.

§ 7. Isotopes in Catalysis

a) General kinetic and specific problems of catalysis

The research directions and problems discussed in the preceding sections are relevant to the study of catalysis, and the general methods considered are applicable to catalytic processes. Therefore it was possible, in the first half of this chapter, to consider catalytic and noncatalytic reactions together without a sharp boundary drawn between them. However, in addition to problems common to all chemical kinetics, catalysis has its own specific problems not met in studies of noncatalytic reactions or not very characteristic of the latter.

These problems include: 1) the nature of the participation of the catalyst atoms in the catalyzed process; 2) the elementary catalytic mechanism and its relationship to the electronic structure of the catalyst and to the type of the catalyzed process; 3) the nature of active catalyst surfaces and closely related problems; 4) modification, 5) poisoning and 6) preparation of catalysts. This category also includes 7) the interrelationships of adsorption and catalysis; 8) the geometrical correspondence between the structure of the catalyst surface and of the catalyzed molecules, and other problems. Accordingly, catalysis has its own range of applications of isotopes in addition to those related to general kinetics.

b) The manner of catalyst participation in a catalytic process

The numerous individual hypotheses concerning the mechanism of the primary action of catalysts on reactions may be reduced to a small number of basic variations.

The first of these is deformation of the substrate molecules at the catalyst surface. The simplest example of deformation catalysis is the catalysis of the ortho–para hydrogen conversion by paramagnetic substances. A second example is the catalytic influence of cations on the decomposition of anions of salts of unstable oxy-acids in the solid phase, such as the influence of Li^+ or Ni^{2+} ions on the decomposition of the MnO_4 ion [105, 106], of Zn^{2+} and Ag^+ on the decomposition of chlorate ions, etc.

The second type of primary catalytic action is transfer of electrons, atoms, or atomic groups by the catalyst. Essentially this consists of the transfer, at some stage of the reaction, of electrons, atoms, or atomic groups from the catalyst to the substrate molecules, and the return of these (or other) electrons, atoms, or atomic groups at other stages.

The third type is induction or initiation of reactions by means of active forms, produced by interaction between the catalyst and the substrate. Often, but by no means always, in reactions of the second and third type one difficult stage which requires a large activation energy without catalysts, is replaced by two or several easier stages effected by means of the catalyst and therefore proceeding with lower activation energies. For catalysis by the transfer and intiation types, the Hinshelwood concept of a decrease of the activation energy under the action of the catalyst ceases to be obligatory as, on the one hand, acceleration of the reaction by a lengthening of the chain with an increase of the observed activation energy is possible in some instances, and, on the other hand, even when the observed activation energies of catalytic reactions are lower than those of noncatalytic, there is usually no lowering of the activation barrier, but a simple reaction path with high energy levels to be overcome is replaced by another, more complex path with a larger number of lower levels. Most of the recent monographs ignore this in discussions of catalysis [25, 107, 108].

A lowering of the original barriers without a change of the reaction stages is possible only in the less common type of deformation catalysis, but even then this kinetic mechanism is not obligatory, as deformation on a catalyst can also lead to replacement of the initial difficult path by a new and easier one.

Verification and study of the initiation of catalytic reactions and their stages by isotopic methods do not differ in principle from the same operations for noncatalytic reactions, although the actual nature of the stages in the process may be very different. We shall return to this topic later in our discussion of research on catalytic chain reactions. Isotopes have so far not been used for verification of deformation mechanisms. We will therefore merely draw attention to the theoretical possibility of using the magnitude of kinetic isotope effects to determine the nature of the deforming action, and will consider in greater detail the prospects and results of isotopic studies of the mechanism and transfer locations in catalysis for oxidation reactions.

In catalytic oxidation the electron transfer mechanism is very common. If this mechanism completely determines the rate of the process, kinetic isotope effects should be absent. Oxidation-reduction reactions of ions in solution form a characteristic region of electron transfer processes. However, as was pointed out in Chapter III, electron transfers in such reactions are usually associated with reconstruction of the solvate layers, and this accompanying process may lead to isotope effects.

It may be possible to detect the catalytic action of ions of a definite charge on a chemical process of this type by intensification of exchange with ions of the same element of higher or lower valence. It would also be interesting to detect and study isotope effects in isotopic exchange reactions of ions by an electronic mechanism, by effecting the process with two or several tagging isotopes. This method could also in principle be applied to confirm the existence of an electronic mechanism in heterogeneous gaseous isotopic exchange reactions.

Isotope methods have been used much more extensively to study the role of oxygen atom transfer on oxidation by gaseous oxygen. The gaseous oxygen (as individual atoms or activated molecules such as $-O_2-$, O_2, etc.) should, for some average time τ, combine with the catalyst, and then react with the oxidized substance as integral chemical constituents of the catalyst.

The meaning of such transfer can be explained by the example of the catalytic oxidation of hydrogen by molecular oxygen, for which such mechanisms are assumed by many authors even at the present time. The transfer stages on oxide catalysts may be represented by Scheme (50)

$$\left.\begin{array}{l} Me_nO_m + H_2 \rightarrow Me_nO_{m-1} + H_2O; \\ Me_nO_{m-1} + \frac{1}{2}O_2 \rightarrow Me_nO_m. \end{array}\right\} \qquad (50)$$

For oxidation in presence of metals, similar schemes, such as (51) have been postulated since the time of de la Rive [109] and Khodnev [110]:

$$\left.\begin{array}{l} n\,\mathrm{Me}+\frac{1}{2}\mathrm{O}_2\rightarrow \mathrm{Me}_n\mathrm{O};\\ \mathrm{Me}_n\mathrm{O}+\mathrm{X}\rightarrow \mathrm{XO}+n\,\mathrm{Me},\\ \text{or}\\ \mathrm{Me}+\mathrm{O}_2\rightarrow \mathrm{Me}\left\langle\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}\right.\xrightarrow{2\mathrm{X}}2\mathrm{XO}+\mathrm{Me},\ \text{etc.}\end{array}\right\}\qquad(51)$$

Such schemes have been postulated for the oxidation of carbon monoxide and sulfur dioxide, the decomposition of hydrogen peroxide, etc. Some authors have regarded the solid oxides which appear in such schemes ($\mathrm{Me}_n\mathrm{O}_m$, $\mathrm{Me}_n\mathrm{O}_{m-1}$, etc.) as special phases, others, as surface compounds. In some instances they were assumed to have the properties of true oxides, and in others the properties of peroxides, but the fundamental idea of transfer was retained unchanged.

Investigation of the structure of simple oxides and their oxygen isotope exchange excludes the possibility of simultaneous coexistence of different fixed oxygen bonds in most typical simple oxide catalysts used in reactions of the oxidation–reduction type. Therefore, when oxygen transfer occurs, the isotopic composition of the oxygen in the water formed at any given instant in Reactions (50) and (51) should coincide exactly with the isotopic composition of the oxygen in the catalyst. This can be easily verified with the use of O^{18}. Agreement of the isotopic compositions of the catalyst and the water would prove that the atomic transfer schemes are correct. Sharp differences between the isotopic compositions of the oxygen in the water and the catalyst, with a correct experimental procedure, could prove conclusively that catalysis by an atomic transfer mechanism does not occur.

By studying the oxygen isotope composition in the oxidation of hydrogen and carbon monoxide over tagged oxide catalysts; S. M. Karpacheva and A. M. Rozen [111] concluded that transfer occurs. These studies were carried out at relatively high temperatures, and certain experimental circumstances which might cause additional isotopic exchange not related to catalytic oxidation were disregarded. The opposite conclusion was reached by D. M. Vainshtein and B. A. Turovsky [112] in a detailed study of the effect of water on isotopic exchange and on the distribution of heavy oxygen in the oxidation of carbon monoxide over manganese dioxide and copper oxide.

Water poisons the catalyst in the oxidationof CO over active oxides. Vainshtein and Turovsky showed that isotopic exchange of oxygen is greatly accelerated by water which, as is known, sharply retards oxidation at low temperatures. This indicates that the observed exchange is not related to the catalytic process. After eliminating the side reaction of oxygen exchange by thorough drying, these authors showed that the low-temperature oxidation of carbon monoxide over carefully dehydrated highly active manganese dioxide preparations is not accompanied by any appreciable transfer of catalyst oxygen to the reaction products [112]. This excludes the trivial chemical transfer mechanism postulated by Benton and others [113] for this system, and permits a conclusive choice to be made between the two chemisorption mechanisms for the process which were postulated in the 1930's on the basis of studies of the kinetics of the reaction and its stage mechanism [114, 115]. Preference must be given to the scheme in which the carbon monoxide in its initial active "presorption" stage does not include the catalyst oxygen, and the latter is not detached from the catalyst at any stage in the process. According to this scheme, even brief and local reduction of the catalyst surface does not occur in catalysis.

The sharp discrepancy between the results of these two isotopic investigations led to a discussion on which the views of Vainshtein and Turovsky were shown to be correct [112]. In this, the detailed investigations of V. N. Vasilyev, S. Yu. Elovich, and L. Ya. Margolis [116, 118], with the same catalyst, were decisive. In this work, in order to obtain conclusive results, the state of the catalyst and the fraction of the acting surface were carefully standardized, and full account was taken of the results of earlier quantitative kinetic investigations [117]. The state of the catalyst and of the adsorbed carbon monoxide was controlled by variations of the electrical conductance of the semiconductor catalyst. The authors showed very convincingly the absence of any appreciable participation in the catalysis either of oxygen from within the lattice or of surface oxygen; the latter is true both for a heterogeneous surface, in which highly active regions operate predominantly, and for a surface "homogenized" by destruction of regions with increased activity. This also conclusively proved the possibility of rapid low-temperature oxidation over oxide catalysts without transfer of catalyst oxygen.

In connection with the results obtained by Vasilyev, Elovich, and Margolis, mention should be made of our work on the bromination of benzene over zinc bromide and the isomerization of α-bromonaphthalene to β-bromonaphthalene over aluminum bromide [119], which led to a similar conclusion, that there is no obligatory transfer of catalyst bromine or all or most of the brominated or isomerized molecules, respectively. Thus, the investigations carried out to date with tagged oxide catalysts have shown that the role of atomic transfer in catalysis is considerably smaller than was formerly believed. At the same time, the results of isotopic investigations indicate the decisive role of reversible electron transfer between the catalyst and the reactants in catalytic oxidation. Catalysis often commences with electron transfers, which lead to formation of special active forms with odd numbers of electrons, corresponding to our "presorption" state and to the surface radicals of N. N. Semonov, F. F. Volkenshtein, and V. V. Voevodsky [120, 121].

In view of the theoretical importance of the question of oxygen transfer in the theory of catalytic oxidation, there is no doubt that investigations with the use of heavy oxygen will continue, with inclusion of new reactions and new catalysts. Meanwhile there has been some clarification of the question of oxygen atom transfer in the catalytic decomposition of aqueous hydrogen peroxide solutions over oxides. The experiments of Taube and others with the use of hydrogen peroxide tagged with O^{18} showed that the catalyst oxygen is not transferred and oxygen of the water also is not involved in the decomposition [122]. These results, in connection with the properties of the catalysts used and the reaction kinetics, led to the conclusion that the decisive role is played by electron transfer between $\mathrm{H_2O_2}$ (or $\mathrm{HO_2^-}$) and the catalysts, which are electronic conductors. The intermediate active form consists of labile charged $\mathrm{O_2^-}$ radicals [123]. This ionic radical is also the principal intermediate active form in the oxidation of $\mathrm{H_2}$ over metals [124]. Thus, study of the role of oxygen atom transfer is naturally bound up with the question of special intermediate active forms in heterogeneous catalysis. Similar investigations are also possible and desirable for catalytic reactions of many other types.

c) Chain reactions in catalysis

The discovery of chain mechanisms in photochemical [125] and thermal gaseous reactions [126] led to searches, lasting many years, for chain mechanisms in heterogeneous catalysis. For a long time chain mechanisms in catalysis were identified with passage of the catalyzed reaction from the solid surface into the volume of the gas or liquid. The possibility of this extension of a mechanism predominant in gaseous thermal chain reactions to heterogeneous catalysis was studied in many systems by means of specially developed methods [127-129], and has been theoretically analyzed in detail.

It was found that initiation of catalytic reactions by the contact surface with passage of the process into the volume is not typical of good catalysts in their normal utilization conditions. The range of heterogeneous–homogeneous reactions in catalysis is very limited, and when they can be detected they usually introduce only small corrections into the main process, which does not leave the surface. The controversial question of the possibility of chain reactions occurring without removal from the catalyst surface and entry into the volume [130] has been studied much less. To solve this question it is natural to make use of isotope methods, by means of which it is possible, under favorable conditions, to distinguish between initiation and propagation of the process.

The first successes in this direction were achieved in relation to the catalytic hydrogenation of carbon monoxide by the Fischer–Tropsch–Orlov process [131, 132]. A great variety of products – hydrocarbons, alcohols, aldehydes, etc. – can be obtained from binary mixtures of carbon monoxide and hydrogen by the action of different catalysts with variations of the external conditions. The number of reactions which can be effected in this way is greatly increasing, and the selectivity of the processes is increased by the use of ternary and more complex gaseous mixtures containing, in addition to CO and $\mathrm{H_2}$, also olefins, ammonia, and other compounds. The mechanism which has been studied most is that of the formation of mixtures of saturated alkanes of normal structure over metallic promoted catalysts; this is the basis of the industrial production of motor fuels from water gas.

In the synthesis of hydrocarbons from water gas, mixtures of all homologous hydrocarbons from methane to heavy paraffins with many tens of carbon atoms in the molecule are obtained [133]. The formation of such large molecules in a single nonchain reaction appears to be impossible. There remains the choice between schemes consisting of series of independent consecutive simple reactions, and schemes with chain polymerization or condensation with participation of the catalyst. If the second hypothesis is valid, the process begins with the formation of some primary active form (initiation), which then develops by a chain mechanism until termination, which concludes the chain growth of the hydrocarbon skeleton by conversion into the final stable hydrocarbon [134]. By this mechanism hydrocarbon molecules of various sizes can be formed from one initial center. Therefore, if the process is initiated by means of tagged organic molecules, either the same contents of the tagged isotope in hydrocarbon molecules of different sizes, or a slow increase of this content with increasing molecular size, is to be expected. If simple consecutive reactions predominate such a result is impossible, and a constant or nearly constant specific content of the atoms of the tagged compound in the reaction products should be found. In other words, in the ideal case, with the first mechanism the molar content of the tracer isotope (C^{13} or C^{14}) introduced for initiation should be constant in hydrocarbons of different molecular weight, while the specific content of this isotope should be inversely proportional to the molecular weight. In the second ideal case the specific content should be constant, while the molar content should increase in proportion to the molecular weight.

The first experiments on this were performed by Emmet and Kummer [135] who used tagged alcohols from CH_3OH to C_4H_9OH for initiation of the reactions. The experiments were carried out under atmospheric pressure at 210-243°C with iron catalysts of the composition used for ammonia synthesis. All the individual hydrocarbons with more than two C atoms in the molecule (C_3H_8, C_4H_{10}, etc.) and all the averaged fractions of high molecular weights were found to be radioactive with constant molar radioactivity and a specific radioactivity which decreased by the hyperbolic law $\rho = \rho_0/n$ with increase of n, the number of carbon atoms in the molecule. This completely corresponds to the ideal distribution with a chain mechanism.

The iron catalysts used by the American workers in their experiments under atmospheric pressure cannot be regarded as typical catalysts for hydrocarbon synthesis. Because of this, and of doubts of the applicability to metals of the Storch-Golumbic-Anderson dehydration–condensation mechanism [134], supported in this investigation, O. A. Golovina, S. Z. Roginsky, M. M. Sakharov, and Ya. T. Eidus carried out a similar investigation with the use of cobalt–thorium catalysts, the classic catalysts for this reaction [136].

For all hydrocarbons except methane* and the C_2, C_3, and C_4 fractions, the distribution of C^{14} with the use of cobalt catalysts was approximately the same as the experiments of Kummer and his associates. This is shown in Table 106.

TABLE 106

Specific and Molar Radioactivities of Various Hydrocarbons Formed with a Cobalt–Thorium Catalyst T 195°C; $(H_2):(CO) = 2:1$ [136]

No. of C atoms in the molecule (average no. of C. atoms in fraction)	Molar radioactivity, mc /mole	Specific radioactivity, mc /g-atom C
CH_4	0.13	0.13
C_6	0.48	0.08
C_8	0.46	0.06
C_{13}	0.46	0.035
C_{19}	0.49	0.025
Original ethyl alcohol	8.4	4.2

The results in Table 106 are a serious argument in favor of a surface chain mechanism for the formation of hydrocarbons from CO and H_2. The constant molar activity of the hydrocarbons formed is nearly 20 times less than the molar activity calculated for a chain process completely initiated by the alcohol. The possibility is not excluded that this factor 20 is the partial or total result of chain multiplication. Still more probable is the induction of new reactions by the growing polymerization chains in the catalytic hydrocondensation of olefins in presence of small amounts of carbon monoxide by the Eidus method [138]. By using tagged carbon monoxide and varying the percentage contents of the initiating addition (alcohol in one case and CO in the other) over

wide limits, it is possible in principle to test for the existence of chain transfer in the reaction and to study its characteristics.

d) Active forms of heterogeneous catalysis

Catalytic reactions are more numerous than noncatalytic, and their types are more varied. Solids of the most diverse chemical compositions and of all known types of electronic structure are used as catalysts, the phase conditions are also extremely varied. This diversity of systems and conditions should correspond to a diversity of the types of active intermediate forms in the reactions. Because of the heterogeneity of the surfaces of most solid catalysts in the chemical and energetic senses, different active forms may exist simultaneously on a surface. If the passage of the catalytic reaction into the phase volume can be neglected, catalytic reactions are concentrated in thin monomolecular layers in direct contact with the solid surfaces. Of this zone, only a part, often very small, actively participates in the reaction, and this causes additional difficulties in an already difficult problem – study of active intermediate forms by direct methods. Therefore any possibility of obtaining even partial, but reliable information about these forms in catalysis is especially valuable from the theoretical aspect. We shall consider, with the aid of examples, the possible contribution of isotope methods to the solution of this most difficult problem.

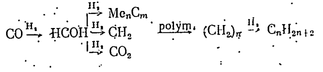
Mechanism of the synthesis process.

All the schemes suggested to explain the mechanism of this process assume the intermediate formation of unusual active forms. According to Fischer and Tropsch [132], Craxford and Rideal [137] and others, the process commences with the formation of phase metal carbides, which are subsequently hydrogenated by hydrogen to give methylene radicals. The latter polymerize to give unbranched hydrocarbon chains

$$Me + CO + H_2 \rightarrow \underset{\text{carbide}}{MeC} \xrightarrow{H_2} Me(CH_2) \xrightarrow{\text{polym}} Me(CH_2)_n \xrightarrow{H_2} Me + C_nH_{2n+2}$$

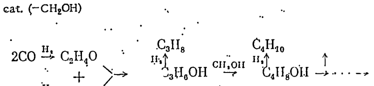
The participation of phase carbides in this scheme seems doubtful, as topochemical reactions are usually considerably slower than reactions in adsorption layers. The possibility of accumulation of large numbers of methylene groups on the surface is also doubtful.

According to N. D. Zelinsky and Ya. T. Eidus [139], carbides are side products; and oxygen-containing formyl radicals are initially formed, subsequently converted into methylenes



$$CO \xrightarrow{H_2} HCOH \begin{cases} \xrightarrow{H_2} Me_nC_m \\ \xrightarrow{H_2} CH_2 \xrightarrow{\text{polym.}} (CH_2)_n \xrightarrow{H_2} C_nH_{2n+2} \\ \xrightarrow{H_2} CO_2 \end{cases}$$

According to Storch, Golumbic, and Anderson [134], the chains involve alcohol radicals, and according to Kummer it is necessary to distinguish between the primary process of initiation of a surface chain, which yields an adsorbed ethyl alcohol radical cat. ($-C_2H_4OH$), and the growth of this radical by dehydrative condensation with methyl alcohol radicals cat. ($-CH_2OH$)



$$\left.\begin{array}{c} 2CO \xrightarrow{H_2} C_2H_4O \\ + \\ CO \xrightarrow{H_2} CH_2OH \end{array}\right\rangle \rightarrow \overset{\overset{C_3H_8}{\uparrow H_2}}{C_3H_6OH} \xrightarrow{CH_2OH} \overset{\overset{C_4H_{10}}{\uparrow H_2}}{C_4H_8OH} \overset{\uparrow}{\rightarrow} \cdots \rightarrow$$

V. V. Voevodsky and N. N. Semenov [140] recently modified this scheme, substituting unsaturated for saturated growing alcohol radicals. In order to design a radical chain scheme, they had to introduce additional unsaturated alkyl radicals, to eliminate a special initiation stage, and to assume growth of unsaturated radicals by addition of carbon monoxide

$$CO \xrightarrow{H_2} H\dot{C}OH \xrightarrow{H_2} \dot{C}H_2 \xrightarrow{CO} \dot{C}H_2\dot{C}O \xrightarrow{H_2} \dot{C}_2H_3OH \rightarrow$$
$$\rightarrow \dot{C}_2H_4 \xrightarrow{CO} C_3H_5\dot{C}O \xrightarrow{H_2} \dot{C}_3H_6 \xrightarrow{CO} \cdots \rightarrow$$

---

* According to our results, CH_4 obtained with a cobalt–thorium catalyst has a fairly considerable C^{14} content, while according to Kummer et al. the C^{14} content of CH_4 is negligible with an iron catalyst.

In this scheme, polymethylene biradicals C_2H_4, C_3H_6, etc. which have retained one free valence alternate with carbonyl and alcohol radicals with one free valence. Direct proof is, of course, needed of the possibility of formation and correct alternation of three such strongly unsaturated forms without appreciable conversion into olefins and alcohols.

A common feature of all these schemes is the intermediate formation of active intermediate surface forms containing several (or many) carbon atoms. This assumption is confirmed by the high contents of polydeuterated hydrocarbons in the isotopic exchange products. However, these results are equally compatible with the polymethylene and alcohol radical hypothesis, and also with the carbonium ion hypothesis.

Synthesis in presence of catalysts containing carbides tagged with C^{14} showed the possibility of carbide chain initiation, but at an insufficient rate. This is not quite conclusive because of the possible decreased activity of previously prepared carbide, but it appears that the carbide route is not the main one. The experiments with tagged alcohols mentioned above [135, 136], which yielded mixtures of hydrocarbons with constant molar radioactivities in the different components, indicate that alcohol radicals are involved in the process. However, in view of the easy hydrocondensation of olefins, it is also necessary to exclude the possibility of primary formation of olefins. Commencement by way of olefins and of alcohols is in equally good agreement with isotopic data, but these are difficult to reconcile with the start of the process as postulated by Voevodsky, Volkenshtein, and Semenov, since in its initiating action methyl alcohol cannot replace the ethyl and other homologs. Thus, isotopic investigations of the synthesis process already give a definite idea of the nature of the intermediate active forms. However, there have been only a few studies of this process with the use of hydrogen and carbon isotopes, and their number bears no comparison with the number of ordinary kinetic and structural investigations of this system. It is therefore possible to take an optimistic view of the future prospects of further application of isotopes to studies of the mechanism of this reaction and of other catalytic reactions of greater complexity.

Mechanism of olefin hydrogenation.

Isotope methods have been applied for a considerably longer time and more systematically in studies of the mechanism of olefin hydrogenation. It is enough to mention the work with heavy hydrogen which has been continued for about 30 years by the Farkas brothers, Rideal and his school [141, 142], and Polanyi and Horiuti and their associates [143]. The systematic character of the investigations, together with the relative simplicity of the process, have made it possible to carry out a deeper analysis of the process than in other cases, and have clarified a number of finer points in the mechanism which are as yet unattainable for alcohols. Thus, by the use of deuterium it proved possible to reject the Born and Franck tunnel mechanism of hydrogenation and to show that each hydrogen atom participates independently in the hydrogenation, i. e., dissociation precedes hydrogenation. By means of isotopic data it has been possible to establish the true position of the association mechanism postulated by Horiuti , Polanyi, and Rideal, and the dissociation mechanism of the Farkas brothers [144]. In the first of these, the process begins with chemisorption which proceeds with rupture of the double bond in the olefin and formation of a "polyhydrogenated" adsorbed alkyl radical. In the dissociation mechanism, catalysis begins with dissociative adsorption of an unsaturated acetylide radical and a hydrogen atom. Studies of deuterium distribution have made it possible to choose between independent and interrelated addition of each of the hydrogen atoms in the molecule, to determine more precisely the number of regions of the catalyst surface for each olefin molecule, and the nature of distribution of hydrogen (deuterium) between them. The use of isotopic determinations in conjunction with kinetic studies led to a substantiated scheme in which the sequence of the individual stages, the role of chemisorbed and free gaseous particles in each, etc., is clearly shown.

The diverse possibilities inherent in isotope methods are very well illustrated by the results obtained by Anderson and Kemball on the orientation of hydrocarbon molecules on metal film surfaces. In §6 of the previous chapter mention was made of the Cambridge work on isotopic exchange of deuterium on metal films [145], which has yielded a wealth of data on the kinetics of complicated exchange. In an investigation of the isotopic exchange of cyclopentane and cyclohexane with deuterium on a number of the transition group metals [146], it was found that half of the hydrogen atoms were exchanged rapidly and the rest considerably more slowly. This is illustrated by the small selection of data in Table 107. The first two lines in this table give the results of exchange with a distribution maximum for molecules with equal contents of D and H, i. e., for $C_5H_5D_5$ in the case of cyclopentane and $C_6H_6D_6$ in the case of cyclohexane. The third line is an example of distribution with a sharp predominance of the monosubstituted product $C_6H_{11}D$ and a rapid decrease in the contents of the forms with increasing numbers of deuterium atoms in their molecules. The distribution curves and their variations with increasing temperature and contact time are difficult to explain other than by the following model scheme: on a number of surfaces the cycloalkane molecule lies parallel to the surface, and is bound to it at two points. Half the hydrogen of the plane-situated carbon ring readily exchanges with deuterium. The change of the doublet to which the molecule is linked also occurs easily, and therefore also a change of the carbon atoms linked to the surface, so that new hydrogen atoms are drawn into the exchange. If the temperature is not too low, after some time half the total H atoms of the hydrocarbon are replaced by deuterium. For exchange of the other half, the molecule must be "turned upside down," which requires an additional activation energy of 4-8 kcal/mole. By means of this model, with the detailed form of the molecule taken into consideration, the authors obtained quantitative agreement between theory and experiment. Their results modify the multiplet theory on the nature of the bonds between cyclic hydrocarbons and the surface. In particular, application of this type of analysis to the hydrogen exchange of benzene on Ni and Pt [147] showed the predominance of dissociative adsorption of phenyl radicals. It is not possible here to give other results which contribute to the detailed scheme for the stages of catalytic hydrogenation on metals, and we must refer to the latest publications of Jenkins and Rideal [148], and to the previously cited paper by Douglas and Rabinowitch, which give a clear idea of the present position of the problem.

TABLE 107

Distribution, by Degree of Substitution, of the Primary Exchange Products in Cyclopentane and Cyclohexane

Catalyst and hydrocarbon	T, °C	Fraction of molecules with different numbers of D atoms											
		D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}	D_{11}	D_{12}
Cyclohexane on oriented Rh	0	0.101	0.060	0.070	0.076	0.106	0.370	0.038	0.033	0.030	0.030	0.036	0.056
Cyclopentane on Pd	0	0.240	0.127	0.066	0.048	0.265	0.007	0.007	0.048	0.039	0 15.3	--	—
Cyclohexane on Rh	-34.5	0.881	0.067	0.020	0.018	0.008	0	0	0	0	0	0	0

§ 8. Isotope Methods for Investigation of Catalysts

Much information is available on the relationship between the catalytic action of solids and special "active" structures. This has led to the active surface concept, in the development and theory of which the role played by Taylor [149] is particularly great. At the present time there are no generally accepted views on the nature and properties of active surfaces. Even Konovalov [150] referred to the connection between catalytic activity and excess free energy. This idea has been developed by a number of modern authors [151-154]

At the same time there is no lack of publications which identify active forms with equilibrium fluctuations of the structural lattice elements [155] caused by thermal motion. Some authors correlate activity with definite elements of crystalline structure [156, 157], others with amorphous formations [158], others with local and microscopic variations of chemical structure caused by stoichiometric deviations and impurities [159], and others with free electrons and holes or free valencies [140]. According to some authors, catalytic activity is a substantive property of solids, and to others, it is a structure-sensitive property. Discussions of these questions are often of an academic nature owing to the lack of direct data on the detailed structure of surfaces, and to the tendency of the supporters of most viewpoints to excessive generalization and extension to all catalysts and all reactions. In reality the several types of elementary processes in which molecules are activated by catalysts, corresponding to the main classes of catalytic processes, probably correspond to an equal or greater number of structures which act as catalytic active centers. Despite the use of a wide range of adsorptional, structural, electronic, magnetic, and electrochemical methods for the study of active contact surfaces, the successes achieved are not great, and the obscurity which remains in this question considerably hinders the development of the catalysis theory as a whole. This raises the need for a search for new methods for determination of the nature of active surfaces

Possible applications of isotopes in catalyst studies were reviewed in ourpaper published in 1940 [160]. Apart from the earlier generally known methods for surface measurement by the Paneth and Vorwerk [161] and Hahn [162] methods, which have retained their importance to the present day,* this paper pointed out:

1) the potentialities of radioactive isotope methods for studying the microchemistry of prepared contact catalysts and for following the addition of impurities during preparation;

2) the desirability of using values of rates of isotopic exchange between atoms on the catalyst surface and gases and ions in solution for characterization of active surfaces;

3) the possibility of adsorption studies at ultra-low degrees of surface covering and the significance of such studies in determination of the nature of active surfaces;

4) the possibility of studying the topographic distribution of the components in complex catalysts (coated, promoted, etc.) and also of catalyst poisons.

In the subsequent 15 years the experimental material obtained has confirmed the reality of these four directions, and new methods of isotopic approach to the solution of the problem have appeared.

Various workers have studied catalyst microchemistry in relation to the active surface problem and the nature of the elementary stages of catalysis. For example, in the investigations, described in the preceding section, of the participation of hydrogen from acid catalysts in the process, in some cases the activating role of small amounts of water introduced into the catalyst was also studied.

N. E. Brezhneva and S. N. Oziraner [163] and G. M. Zhabrova et al. [164], in studies carried out in our laboratory, investigated the effects of small additions of PO_4^{3-}, SO_4^{2-} anions and Na^+, Pb^{2+}, Zn^{2+} cations on the catalytic properties of metallic and oxide catalysts. In some cases very characteristic modification curves were obtained, with optimum values at very low contents of the additives in the catalyst. Some investigations of the capture of poisons by catalysts, etc., were also made. This work showed that it is possible to use radioactive isotopes for studying the capture and removal of impurities in conditions of any degree of complexity, with a sensitivity not attainable by other methods, and also to determine the stability and nature of such capture. Extensive experimental material is available which confirms the validity of the fourth point of those enumerated above, which is closely associated with the first. Conditions for topographical studies are especially favorable in work with massive monocrystalline and polycrystalline catalysts. By the introduction of a praticular additive, tagged with a radioactive isotope, at a definite point on the surface of such a catalyst, it is possible to use one of the available well developed methods to follow the displacements of the additive. For example, in the case of substances with weakly penetrating radiations (α- or soft β-emitters), the known coefficients of absorption of these substances by the material can be used to study the rate of penetration into the massive specimen by the weakening of the radiation emitted by the substance applied to one of the external surfaces. Examples of such measurements are found in Hevesy's older papers [165] on the diffusion of radioactive lead, in recent work by A. N. Murin et al [166], and in many other studies.

When this method is unsuitable because of the high penetrating power of the radiation or, on the contrary, because of diffusion to distances at which the radiation is difficult to measure, the specimen is divided into a number of plane layers at right angles to the presumed direction of diffusion, and the radiation of each is measured. This technique is widely used for studies of phase and chemical transformations in solid state physics and metallography [167]. Both these methods yield average statistical data on the translocation of impurities in solids [168].

The actual topography with all its particular characteristics can in many instances be determined by means of autoradiography. The chemical possibilities of this method, especially in relation to large monocrystals formed in solutions, are discussed in Hahn's well known monograph [169]. Recently, in connection with the development of special photographic materials, microradiographic methods have been evolved by means of which the distribution of a radioactive material in microscopical objects can be determined [170]. Other methods can also be adapted to small objects, but the degree of dispersion of the materials to which they are applicable is generally much lower than the degree of dispersion of active contact catalysts. This should not, however, present a serious obstacle to the use of radiometric methods in studies of the distribution and translocation of additives in the basic material. There is no doubt that catalytic processes on massive solids occur by the same mechanism as on powders. Reliable methods exist for studying these processes on massive catalysts, and therefore it is entirely possible to study in detail the distribution of additives introduced into the catalyst and the course of displacement of these additives on heating and during chemical reactions. Radiochemical methods may also be useful in work with powdered and porous catalysts for determination of the regularity of distribution of added materials between different grains and over different regions and zones of a porous body, and also for porosity studies.

The number of published papers which deal directly with the topographical distribution of added substances in catalysts is not large. In view of the close relationship which has emerged in recent years between the presence of electrons and holes in a solid and its catalytic activity with respect to definite reaction types, and the differences between substances with electronic conductance and hole conductance (Boudart [171], Hauffe [172]), great interest attaches to the possibility of studying the disposition of additives which regulate the type and magnitude of electrical conductance. This has not yet been done for catalysts. However, interesting studies have been made of the distribution and migration of impurities, such as radioactive copper, in germanium. Its electronic properties are appreciably changed by copper even at 1 : 10^6 concentration [173]. Of other researches relevant to catalysis, we may mention the autoradiographic studies of polonium on silver plates, which revealed a nonuniform distribution of the added material and in which the diffusion rate of polonium and its variation with the temperature was measured [174].

After the investigations reported by our association in recent years, the existence of surface "creep" in catalysis can hardly be doubted [175]. In principle, radiography offers a direct method for studying such processes without giving an average for the whole specimen. Thus, it is possible to study the growth of particles of active material on the carrier surface, the creep of promoters over the catalyst surface, and the redistribution of catalyst poisons between different components of multiphase contact catalysts. By means of radiography it is easy to distinguish between volume diffusion through the crystal lattice and intercrystallite diffusion, and to study the topography of the latter and of surface creep. In favorable conditions it might also be possible to carry out radiographic studies of the creeping migration of molecules of the reactants and reaction products over the catalyst surface and in its pores.

With isolated exceptions, these possibilities are not yet being used in special catalytic studies. The position is somewhat better in the use of radiocarbon for studying the kinetics of the formation of the carbon (coke) deposits in many catalytic reactions of organic molecules. In some cases this coke, which consists of highly condensed hydrocarbons with $C:H$ ratios close to 1, merely hinders the reaction by blocking the surface, while in others it assumes some catalytic functions [176]. The work of our laboratory on the catalytic cracking of hydrocarbons containing various additions of tagged olefins and paraffins, constituting a complex reaction mixture, has revealed the role of different types of hydrocarbons in the formation of coke films on the surface of aluminosilicate catalysts, and the influence of external conditions on these processes [49, 50 177]. B. V. Klimenok and A. B. Shekhter [178] have studied the topography of this process by electron microscopy.

Despite isolated successes, the application of isotope methods to studies of the microchemistry of catalysts is in its earliest stages, and the full utilization of the possibilities inherent in these methods is a matter for the future.

In recent years there has been lively interest in the second of the four directions listed at the beginning of this section, namely the study of active surfaces by the rates of isotopic exchange between a catalyst and the reactants. The first observations of the existence of a parallelism between the ease of hydrogen isotope exchange and activity as acid catalysts were made as early as the 1930's. The first observations of a parallelism between halogen isotope exchange in metal halides and their power to catalyze halogenation and isomerization of halogenated derivatives were made at about the same period (see Chapter III). In heterogeneous catalysis, such investigations dealt with hydrogen and oxygen in oxide catalysts used for cracking and isomerization of hydrocarbons, and oxide oxidation catalysts. The results of the early work on solid catalysts are only of historical interest, as important sources of error were disregarded. Later work by Winter [179], Cameron, Farkas, and Litz [180], and others on isotopic exchange of oxides with molecular oxygen showed that in these systems oxygen isotope exchange usually begins at considerably higher temperatures than catalysis, and the oxide sequence by isotopic exchange rates does not coincide with the catalytic sequence. Nevertheless, there is a definite parallelism between

---

* The Paneth-Vorwerk method is based on determination of the limit of rapid isotopic exchange with an electrolyte, which is interpreted as the end of exchange in the monolayer. The Hahn method involves measurement of emanating power for determination of the specific surface.

exchange capacity and catalytic activity of different specimens of the same catalyst. In particular, G. K. Boreskov and L. A. Kasatkina [181] obtained very interesting data on the great acceleration of isotopic exchange of vanadium oxides by additions which increase the activity of this oxide in the oxidation of sulfur dioxide. Similarly, for some cracking and isomerization catalysts there is undoubtedly a parallelism between hydrogen isotope exchange capacity and catalytic activity.

There are various complicating factors in the situation. For example, many volatile oxides, including water and carbon dioxide, exchange more readily than O_2 with solid catalysts, and therefore act as catalytic carriers of oxygen isotope. Similar complications occur in hydrogen exchange. The exchange of atoms in solid surfaces is relevant to catalysis. However, under ordinary experimental conditions it is difficult to exclude exchange of atoms from within the volume of the solid. The rate of isotopic exchange on solid catalyst surfaces is highly sensitive to the action of additives which influence the elementary catalytic process. Apart from the strong antibatic influence of water on the exchange of MnO_2 with O_2 and on the oxidation of CO to CO_2 over MnO_2, mention may be made of the results obtained by McGeer and Taylor [182] on the influence of catalyst poisons on homomolecular isotopic exchange of molecular nitrogen at the surface of rhenium catalysts used for ammonia systhesis. It was shown in this work that amounts of oxygen and water which are not sufficient to have any appreciable influence on the catalytic activity of the metal with respect to nitrogen hydrogenation result in almost complete cessation of isotopic exchange of N_2^{15} with N_2^{16}. No doubt this contains great possibilities for studying the early stages of catalyst poisoning and methods of preventing it, and also for studying the properties of specially active centers present in very small numbers on the surface.

Much work will be required to study the details of the mechanism and kinetics of isotopic exchange for the utilization of these possibilities in investigation of the effects of additives; however, this work will be justified both by the direct results and by the basis it will provide for the development of new methods of evaluating the activity and selectivity of catalysts.

The above examples refer to isotopic exchange between solid contact catalysts and gases. In principle the same technique may be extended to isotopic exchange of catalysts with ions in solution. However, in this case recrystallization and electrochemical complications arise which make it difficult to obtain clear results.

Adsorption determinations with the use of radioactive substances are more sensitive then any other methods. Even in the case of monocrystalline objects, with the use of such long-lived isotopes as C^{14} (which, moreover, is generally used in an isotopically impure state), it is possible to study adsorption and catalytic conversions in layers covering less than 1% of the surface. These possibilities were realized, in particular, recently by Farnsworth [183] and others in the adsorption of carbon dioxide on metallic nickel. This work revealed unusual chemical behavior of carbon dioxide, which decomposes into oxygen and carbon monoxide even at 30°C.

A second example of the use of the high sensitivity of radiochemical adsorption determinations is provided by E. M. Ioffe and B. A. Nikitin's investigation [184] of active carbons by means of radium emanation. The sensitivity of the radiochemical method for studying the adsorption of gases on porous and powdered solids is considerably higher than the sensitivity of the finest modern methods for adsorption determinations by means of the adsorption balance [185, 186].

These possibilities have been used only in some individual investigations without an adequate relationship to catalysis. This offers an extensive new field of investigation. The adsorption of ions from electrolytes with ultra-low degrees of surface covering has been studied much more. Such investigations have been performed on numerous massive materials, powders, and precipitates, with the use of radiostrontium, radiobarium, radioiodine, radiolead, and many other radioactive substances. When applied to prepared adsorbents and catalysts, this method permits studies of physical and chemical adsorption at extremely low degrees of surface covering, when all appreciable interaction between the adsorbed particles ceases. An important fact in relation to the theory of catalysis is that, despite theoretical expectations, such processes do not obey the Henry isotherm, but parabolic logarithmic isotherms; in these conditions this can only be explained by sharp heterogeneity of the most active regions, present in very small numbers.

The four directions which have been discussed do not exhaust the range of application of isotope methods to catalyst studies. Thus, a fifth direction is the possibility of studying the mobilities of atoms in solid catalyst lattices and on their surfaces by the self-diffusion of radiocative isotopes, which is a peculiar diffusional topochemical form of isotopic exchange [167, 168]. In this way it has proved possible to determine quantitatively the self-diffusion of atoms of many elements [187] and the effects of a number of parameters on it. In the case of binary compounds it is necessary to distinguish between the mobilities of the anions and cations. An example of a successful determination of these quantities by radioactivity methods is provided by the work of A. N. Murin et al. [166] on silver halides.

A very promising sixth direction, not yet explored in catalysis, is the study of chemical and phase transformations of solids by their emanating power. To the three natural emanations – radon, thoron, and actinon radioactive inert gases (A, Kr, Xe) formed from their neighbor elements have been added. As was first shown by L. S. Kolovrat-Chervinsky [188], the emanating power of a solid responds very sharply to the slightest changes of its structure, and this makes emanation methods very interesting in principle for studies of catalyst formation.

Until very recently emanation methods had not been applied to studies of catalyst preparation processes. However, processes typical of catalyst formation, sometimes even in systems of direct interest in catalysis, have been studies in connection with the problem of solid phase transformations and hidden changes of fine structure. Mention must be made of the numerous papers by Hahn and his school on the photochemical and phase transformations of solids [189] and on the aging of precipitates [190]. Emanation methods in their perfected form [191] have every reason for being widely adopted for investigations of the formation of active solids: adsorbents, catalysts, electrochemical materials, etc.

However, this does not exhaust the possible applications of isotope methods to studies of catalyst formation. In relation to the above-mentioned role of microchemical additions as regulators of the activity and specificity of catalysts, there is the equally important possibility of using radioactive tracers for studying the amounts, kinetics and topography of the capture of impurities at various stages in the preparation and performance of catalysts. In some instances isotope methods have already provided possibilities of studying the inner mechanisms of topochemical reactions, which form a considerable proportion of catalyst preparation methods. Studies of the elementary mechanism of metal oxidation may be mentioned in this context. One of the most difficult problems in the theory of the formation of solid oxides by the action of oxygen on metals is the mechanism whereby the reaction is able to continue after a continuous oxide film has been formed. Wagner has developed an orderly theory of the motion of metal ions and dissolved oxygen through the oxide layer, which satisfactorily explains most of the kinetic relationships. By this theory, in some cases the oxide layer grows from the outside by reaction between the diffused metal ions and oxygen, and in others, from the inside, by reaction between the metal and oxygen which has penetrated through the oxide film to the metal–oxide interface [192]. The systems studied by Wagner and his school were divided by him into these two groups; oxidation of copper to cuprous oxide was included in the first type. By oxidizing a copper plate tagged with a radioactive isotope and covered externally with a layer of inactive metal, Bardeen, Brattan, and Shockley [193] showed that a film of the oxide of the radioactive isotope was formed on the outer surface in the reaction, thus confirming Wagner's views.

To summarize the above, it can be seen that the applications of isotope methods to individual systems have included all the fundamental types of processes met as completed reactions or reaction stages in the formation of catalysts; namely, the precipitation of sparingly soluble solids from solutions, aging and washing of precipitates, and phase and chemical transformations of solids on heating.

In our laboratory, E. A. Fokina and O. V. Krylov used zinc sulfide tagged with radiosulfur to demonstrate the possibility of successful isotopic studies of changes in catalysts during their operation. The concept that catalysts remain unchanged in catalytic reactions has become obsolete. Peculiar catalyst corrosion may occur, i. e., chemical destruction of catalysts under the influence of catalytic reactions [194]. Added to this, there may be the usual surface and phase chemical reactions of the starting substances, the reaction products, and impurities with the catalyst; finally, flowing gases and liquids may detach considerable numbers of small particles from the surfaces of stationary porous solids to form aerosols and solvesols [195]. In the catalytic decomposition of isopropyl alcohol over zinc sulfide, it proved possible to detect and study the removal of microscopic amounts of sulfur from the catalyst, and also the conversion of some of the sulfide sulfur to sulfate in quantities on the borderline of ordinary analytical determinations, but important in catalysis.

The foregoing directions cover most of the problems confronting research on catalysis. Of a more special character is a new and peculiar direction developed in our association in relation to the position occupied in catalysis by effects produced by surface inhomogeneity, mutual repulsion of adsorbed molecules; and their interaction through the electron hole cloud.

§ 9. Isotope Methods for Investigation of Surface Inhomogeneity and Interaction Between the Adsorbed Molecules

a) Inhomogeneity and repulsion

In the middle of the 1920's, Langmuir, Rideal, Schwab, and others worked out the adsorption kinetics of catalytic reactions, which accounted satisfactorily for their main qualitative characteristics. Augmented by the Taylor concept of activated adsorption, this theory has since occupied a leading position in the theory of catalysis, determining the direction of experimental studies and the methods for the theoretical interpretation of the results. Most investigators have accepted these concepts, despite the paucity and incompleteness of the experimental data on which they were based, and the extreme idealization of the effect in the fundamental postulates. From the beginning of the 1930's Soviet chemists have carried out systematic quantitative investigations of the kinetics of contact reactions and their mechanism, which soon led to the conclusion that the equations of the adsorption theory do not satisfactorily describe the true course of the reactions. The following facts did not fit into the adsorption theory: 1) the exponential variation of the consumption of carbon monoxide with time in catalytic oxidation over oxides [196], which subsequently proved to be a very common phenomenon [197]; 2) the constant fractional exponents in the kinetic equations for ammonia synthesis found by Temkin and Pyzhov [198]; 3) the slow nature of specific activated adsorption, which makes simple summation of the stages impossible, and other data, 4) these invesigations and the electrochemical studies of the A. N. Frumkin school [199, 200] demonstrated the inapplicability of the Langmuir adsorption isotherm, which forms the basis of the Langmuir-Schwab adsorption kinetics, to many systems, and led to the discovery of the logarithmic isotherm; 5) during the same period peculiar anomalies relating to catalyst poisoning and to the kinetics of activated adsorption, requiring special explanation, were discovered. By the end of the 1930's it became possible to explain some of the anomalies by the concept of extensive heterogeneity of catalyst surfaces with respect to heats of adsorption and activation energies. Subsequently, with the use of mathematical statistics, a finalized theory of catalysis and adsorption on widely inhomogeneous surfaces was formulated, which correctly represents the characteristics of adsorption and catalysis on real active catalysts [201].

From 1936 numerous investigations have dealt with the theory of adsorption in presence of repulsion forces between the molecules on adjacent regions of the surface [202, 203]. In 1937 N. I. Kobozev and Yu. B. Goldfeld [204] used the concept of repulsion to explain the anomalously rapid self-retardation observed by them in the desorption of hydrogen from finely dispersed copper.

In 1941, N. I. Kobozev, Yu. B. Goldfeld, and M. I. Temkin simultaneously and independently found that it is possible to derive some of the relationships which follow from the statistical theory of widely inhomogeneous surfaces on the assumption of mutual repulsion of the adsorbed molecules, which increases with increasing surface cover [205, 206] as the result of closer approach.

The possibility of such effects under the influence of electrostatic repulsion in the adsorption of ions on metals was established earlier by Langmuir [207] for cesium on tungsten. However, as a rule the polarization of the molecules of the reactants in the adsorption layers is insufficient for such effects to appear, and therefore the original introduction of the repulsion concept was of a purely heuristic and formal character, and appeared to contradict van der Waals attraction between the adsorbed molecules. It was shown by F. F. Volkenshtein [208], irrespective of the mechanism, that, on the assumption that anomalous adsorption isotherms can result from repulsion, it is possible to derive a definite relationship between types of inhomogeneity and the dependence of the repulsion forces on distance. The possibility of long-range repulsion forces arising in adsorption on semiconductors, caused by the influence of the adsorbed molecules on the electron-hole equilibrium, was demonstrated in the USSR by F. F. Volkenshtein and V. L. Bonch-Bruevich [155, 209]. Hauffe in Germany [170] and Weisz in the United States [210] obtained similar results by means of the electron boundary layer theory, and Schottky [211], from the variation of the electron levels of a solid at the interphases in adsorption. Although it has never been done completely, it seems that all the initial postulates of the statistical theory of adsorption and catalysis on inhomogeneous surfaces may also be obtained for completely homogeneous surfaces in the existence of repulsion forces which regularly decrease the heats of adsorption of all the molecules on the surface with increase of the fraction covered.

Mention must also be made of Boudart's attempts [212] to extend these concepts to metals, and the possibility that a special form of induced inhomogeneity may arise as the result of the influence of an adsorbed particle on the electronic properties of the solid lattice in contact with it [155]. Thus the two concepts – inhomogeneity and repulsion – with their very different physical contents, lead to very similar; sometimes even identical relationships. The choice between them in each individual case, and correct evaluation of their significance in catalysis, are of primary importance. This appeared to be impossible to do conclusively by the usual methods, and therefore the concept began to gain ground that these effects are indistinguishable in principle, and that the distinctions discussed above are merely apparent.

Even at the start of the 1940's it became evident that this controversy could be settled by means of differential isotopic determinations. The idea was put into effect after the end of the war in the form of the differential isotopic method.

b) The differential isotopic method

When mutually repelling molecules are adsorbed on an ideally homogeneous surface, the adsorbed particles at equilibrium tend to be as far apart as possible, without forming pairs and larger groups. For any given degree of surface cover all the adsorbed molecules, to the accuracy of statistical fluctuations, are in the identical state, irrespective of the method and sequence of their introduction onto the surface.

Suppose that practically irreverisble adsorption of carbon monoxide, without separation into atoms, occurs by small portions of different isotopic composition, For example, first a portion of $C^{12}O^{16}$ is adsorbed, then a portion of $C^{12}O^{18}$, and then, successively, portions of $C^{13}O^{16}$, $C^{13}O^{18}$, $C^{14}O^{16}$, and $C^{14}O^{18}$. Even if the existence of O^{17} is ignored, it is possible to apply 6 isotopically different forms of carbon monoxide to the surface. With the assumed homogeneous surface model, the behavior of the molecules of all six portions will be equal, to the accuracy of isotopic corrections, and any part of the adsorbate, removed from the surface by any method, will have exactly the same isotopic composition, corresponding to complete mixing of all the portions. In other words, no "biographical" distinctions are possible in this instance. The position is quite different in adsorption on a biographically heterogeneous surface. In such a case, if the experiment is performed under suitable conditions, molecules of different potitions of the adsorbate may be situated on regions of the surface with different properties; for example, molecules of the first portion on regions with minimum values of activation energy of adsorption or with maximum heats of adsorption, and molecules of the last portion on regions of maximum E and minimum Q.

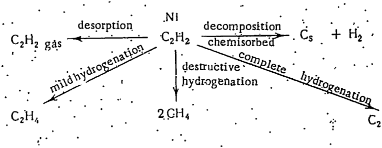
Such a distribution is possible, but not obligatory, as molecules can also be attached at the points of impact with the surface without overcoming the activation barrier, regardless of the value of Q of adsorption [201]. Moreover, secondary mixing of previously distinct portions may occur by isotopic exchange through the gas phase by means of reversible adsorption and desorption, or through the surface by two-dimensional creep, or finally by substitution reactions involving adsorbed molecules only or adsorbed and free molecules. Therefore, loss of individuality by molecules of different portions does not exclude heterogeneity, but individuality can be retained only in presence of heterogeneity. The retention of biographical distinctions in the layer can be proved in different ways. The most direct route would be to show that molecules of different portions are present in different states, by the values of various constants for molecules of different isotopic composition. Such experiments are possible in principle with the use of ordinary and microwave spectroscopy, but are very difficult. Retention of individuality can be tested more simply by differences of reactivity of molecules introduced with different portions. With sufficiently large reactivity differences it may be possible to detect measurable differences in the isotopic composition of different products, or of different portions of the same product, with sharp deviations from the isotopic composition which corresponds to equipartition. For this purpose, use may be made of desorption by small portions, reactions yielding volatile products from the adsorbed molecules, conversion of the adsorbed molecules into other surface chemical forms, etc. The basic idea of the differential isotopic method is adsorption on a surface byportions of different isotopic composition, and measurement of the isotopic composition of consecutively removed portions of the adsorbed material. The weakness of this method lies in the possibility of similar effects with different types of heterogeneity. For example, differences in the isotopic composition of the products are possible not only with microheterogeneity (i. e., with differences in the adsorbent and chemical properties of different regions); but also in presence of several phases or even in presence of pores and capillaries of different accessibility. To avoid the ambiguities which arise, it is necessary to select the experimental conditions suitably, and sometimes to perform special control experiments. The differential isotopic method was first used for the molecular adsorption of hydrogen and deuterium on active sugar carbon [213], no isotope mixing occurred in the adsorbed gas, and during desorption the system, in the first approximation, passed along its original route in the reverse direction. Later, heterogeneity was experimentally established by this method for other systems [214-219], shown in Table 108. The results obtained by other authors are also shown.

TABLE 108

Results of Tests of Energetic Heterogeneity by the Differential Isotopic Method [214-216].

Solid	Adsorbed gas	Result	Type of adsorption	Literature
		Elements		
Active sugar carbon	H_2; D_2	Heterogen	Physical	–
Ni_{met} from oxide reduced by H_2	H_2; D_2	Heterogen	Chemical	–
Fe_{met} with additions	$C^{12}O$; $C^{14}O$	Heterogen	Chemical	[218]
Ni_{met}, by Bag and Egupov's method	$C_2^{12}H_2$; $C^{12}C^{14}H_2$	Heterogen	Chemical	–
Pt_{met} on asbestos	I_2^{127}; $I^{127}I^{131}$	Heterogen	Chemical	–
		Oxides		
ZnO from hydroxide, carbonate, and by oxidation of Zn vapor in the arc	H_2; D_2	Heterogen	Chemical	–
ZnO by pyrolysis of carbonate	$C_2^{12}H_2$; $C^{12}C^{14}H_2$	Heterogen	Chemical	–
ZnO	$C_2^{12}H_5OH$; $C^{12}C^{14}H_5OH$	Heterogen	Chemical	–
Al_2O_3	$C_2^{12}H_5OH$; $C^{12}C^{14}H_5OH$	Heterogen	Chemical	–
SiO_2	CO_2; $\dot{C}O_2$	Heterogen	Chemical	[219]

Surface heterogeneity was discovered in all 10 systems studied by the differential isotopic method. In two cases, in the opinion of the author [216], the observed effects for zinc oxide and aluminum oxide cannot be completely explained by heterogeneity but indicate simultaneous repulsion effects. Without discussing the reasoning, which does not appear to be irreproachable, we may note that, up to the present, homogeneity has never been found by this method. The fractions of special surface regions detected in various systems by the differential method vary in very wide limits from fractions of one percent to several tens of percent. It is probable that in some instances some of the surface heterogeneity eluded observation because of subsidiary redistribution processes. In these examples quantitative biographical differences in the values of the activation energies of desorption were found by the differential isotopic method. Of more direct relevance to catalysis are the qualitative reactivity differences of molecules adsorbed in portions of different isotopic composition. Experiments in this direction were carried out by N. P. Keier [220] on acetylene tagged in the carbon, over nickel catalysts; the isotopic carbon composition of each of the five different products shown below was determined separately



Molecules of the middle and last portions are predominant in the desorbed acetylene. The carbon in decomposition and methane in destructive hydrogenation are formed only from the very first portions of acetylene. Ethylene and ethane are formed predominantly from the middle portions. It is not possible here to analyze the results of this interesting investigation in detail, but we must stress that its results conclusively prove the qualitative biographical heterogeneity of the Ni surface by its catalytic properties.

Despite its clarity and simplicity, the differential isotopic method has a number of defects: 1) the heating needed for desorption can easily cause redistribution of the molecules; 2) the degree of surface cover changes during desorption, and this may make it difficult to discriminate between effects of different types with interaction in the layer; 3) the method does not give the form of the distribution functions. These defects can be eliminated if the basis of heterogeneity investigations is isotopic exchange of adsorbed molecules with molecules of a gas or solution. This method, without allowance for the laws of complicated isotopic exchange discussed in Chapter V, was first used in purely qualitative form by Eischens [221] as a logical development of our differential isotopic method. Carbon monoxide and metallic iron catalysts were used. Differences in the isotopic composition of the oxide exchanging under different conditions served to prove heterogeneity of the system. This eliminates only the second defect of the method, since the exchange occurs at constant degree of surface cover. However, kinetic isotopic exchange determinations can be used in principle as the basis of a quantitative method for studying heterogeneity. For this, it is first necessary to adsorb a substance of definite isotopic composition, and then to cause it to exchange isotopically with the same adsorbate of different isotopic composition, contained in a gas or solution. The kinetic exchange isotherms and the calculation methods described in Chapter V can then be used to determine the form of the distribution function of the exchange activation energies, which in the simplest case coincides with the distribution function of the heats of desorption. Investigations in our laboratory showed that such determinations are quite feasible. They can be augmented by kinetic curves of isotopic exchange from surfaces covered with an adsorbate introduced in portions of different isotopic composition.

In principle, the kinetics of isotopic exchange between atoms in a catalyst surface and a substance in a phase of variable composition can also be used to decide between homogeneity and heterogeneity; for example, by the isotopic exchange of oxygen in oxide catalysts with gaseous oxygen, dissolved Zn^{2+} ions with ZnO, or Cu^{2+} with metallic copper. Essentially any carefully plotted curve for the isotopic exchange of a solid, below the limiting value corresponding to a monolayer, in specific surface determinations by the Paneth method, can be used for determining the statistics of a surface. Experimental difficulties arise which we shall not discuss here.

To the three isotope methods for studying inhomogeneity discussed above, a fourth should be added, which was mentioned in Chapter IV; this consists of studies of changes of thermodynamic isotope effects of adsorption with degree of surface cover. Thus the problem which appeared to be insoluble can be successfully solved by several different isotope methods; the variations of these discussed here do not exhaust all the possibilities.

This discussion of the applications of isotopes in catalysis shows that new problems and new directions for the utilization of isotopes arise in the transition from homogeneous thermal to heterogeneous catalytic reactions. Chemical reactions in the solid phase have much in common with catalysis in their problems and methods. This wide branch of kinetics, which has an important role in geochemistry and technology, has also its own specific features not met in the use of isotopes in homogeneous kinetics and catalysis. Special problems arise in the use of isotope methods in radiochemistry, etc. It is in general true that, with common basic principles and methods, the application of isotopes to each particular type of process has its own specific characteristics.

§10. Potentialities of the Use of Isotopes for Studying the Reactivity of Matter

The reactivity of matter has long been, under different names, the central problem of chemistry. Most of the quantitative relationships which characterize the chemical properties of individual elements and types of compounds in inorganic, organic, and biological chemistry reflect the reactivity characteristics of these substances. The same category also includes the more general relationships between the direction of a reaction and structure, such as the Markovnikov rule, the Walden inversion, and the Chernyaev trans influence. Reactivity occupies an important place in Werner's coordination theory and the Bronsted-Lowry protolytic theory of acids and bases. Finally, even such generalizations in chemistry as D. I. Mendeleev's periodic law and A. M. Butlerov's theory of chemical structure are primarily concerned with relationships between reactivity and chemical composition and structure. For all their importance and value, these laws cannot be used to predict the quantitative relationships between different reaction directions or to calculate absolute rates of chemical processes from data on composition and structure. Clear information on reaction mechanisms is also lacking. At the present level of chemical kinetics, theoretical calculations of the rates and directions of chemical processes have become possible in principle, and there are many examples of good agreement of calculated results obtained in this way with theory. Therefore, together with the further development of extensive qualitative investigations in organic and inorganic chemistry, chemical kinetics now contains the basis of a quantitative theory of reactivity, the ultimate purpose of which consists of conclusive predictions of the mechanisms, directions, and rates of chemical reactions from known structures of the reactants, and of structure from reactivity.

Isotopic exchange reactions are especially convenient for such investigations, because of the simple kinetics, zero heat effects, and absence of volume changes (see Chapter II). Another valuable feature is the relative ease of determination of the true orders of such reactions in complex cases, examples of which were given in Chapter II and III, and the simple calculations of the absolute rates of reactions of this type. Therefore even now a considerable proportion of reactivity studies is performed with the use of isotopic exchange instead of ordinary chemical reactions, and there is no doubt that the importance of isotopic exchange in experimental studies of this kind will increase with increasing availability and use of isotopic methods.

The transition from ordinary reactions to isotopic exchange, while greatly simplifying theoretical analysis of the results, does not in itself ensure a correct direction of the investigations. The modern detailed theory of reactivity cannot develop without a differentiated approach to reaction stage mechanisms. One of the most general and fundamental questions is the question of the rate-determining stage, because all the quantitative characteristics of a process obtained from a kinetic experiment apply in the first instance to the rate-determining stage. As was shown in Chapter IV, invaluable help is provided here by exact determinations of kinetic isotope effects, the magnitude and temperature dependence of which give what are at the present time the most direct information possible about the structure of the intermediate complexes and the nature of the formed and broken bonds. These effects, and also the numerous methods based on hydrogen exchange studies, provide important data for deciding between molecular and radical or ionic radical mechanisms in determinations of the precise stage mechanisms of reactions, genetic relationships between reaction products, nature of the intermediate active forms; etc. It is probable that the first strictly quantitative laws governing the reactivities of saturated and active molecules will be derived with the aid of isotopic methods, and earlier for isotopic exchange than for ordinary reactions, for which isotopic exchange provides excellent models. The present monograph contains numerous examples of such investigations with isotopic exchange of cations, hydrogen, oxygen, and halogens. A detailed discussion of this question is not possible here, and we restrict ourselves to mention a few examples. G. P. Miklukhin et al. [222, 223] studied in detail the paths of hydrogen transfer in various organic reactions by means of deuterium. I. P. Gragerov [224] used similar methods for studying the possibility of transfer of whole radicals in various organic reactions, and was able to show that such processes develop to an appreciable extent in some instances. Valuable data and general relationships between hydrogen exchange reactivity and electronic structure were obtained by A. I. Brodsky (see Chapter III), and A. I. Shatenshtein (see Chapter III) studied the role of acid–base properties in such exchange and the connection of these properties with chemical structure. Recently A. I. Brodsky [225] made the first attempt to summarize and generalize the available data on reactivity obtained with the use of isotopes.

In concluding this section on reactivity we must stress that the study of this problem is interrelated with the need for more precise information on the atomic and molecular structure of molecules. In this last question isotopes also play a very important part. Because the force constants and geometrical dimensions of isotopic molecules are practically identical, spectra of isotopic molecules can be used for very accurate determinations of the absolute values of force constants characterizing different chemical bonds and different motions of the molecule, and this method is being used with great success in modern spectroscopy [226-228]. Thus, for the successful development of the reactivity theory, research into it should involve extensive and varied use of isotopic methods. This use has so far been inadequate, just as inadequate use has been made of the great possibilities of hot atom chemistry for studies of reactivity in radiochemical processes.

The discussion in this chapter demonstrates the unusually fertile and promising character of isotopic methods for the study of chemical processes, especially when use is made, not merely of the high sensitivity of isotope determination methods, but of specially designed methods which take into account both the specific character of isotopic processes and the nature of the kinetic problems in question. It must be stressed, however, that the successes which have been achieved form only a very promising beginning. Full utilization of the possibilities demands further, more extensive and systematic investigations of individual systems, searches for new and improved methods, and perfection of the theoretical principles in the fields discussed in this book.

LITERATURE CITED

[1] M. Roualt, C. r. 207, 620 (1938).

[2] B. F. Ormont, The Structure of Inorganic Substances, Moscow-Leningrad, State Tech. Press (1950).

[3] W. Koskoski and R. Fowler, J. Amer. Chem. Soc. 64, 850 (1942).

[4] J. Downs and R. E. Johnson, J. Chem. Phys. 22, 143 (1954).

[5] V. Linnenbom, in Radioactivity Applied to Chemistry, Moscow, Foragin Lit. Press, p. 50 (1954).

[6] B. Anderson, Z. phys. Chem. B 32, 237 (1936).

[7] G. Seaborg, Chem. Rev. 27, 199 (1940).

[8] R. C. Thompson, J. Am. Chem. Soc. 70, 1045 (1948).

[9] Ya. K. Syrkin and M. E. Dyatkina, Structure of Molecules and the Chemical Bond, Moscow, State Chem. Press (1946).

[10] C. K. Ingold, Structure and Mechanism in Organic Chemistry, N. Y. (1953).

[11] M. Polanyi and A. L. Szabo, Trans. Far. Soc. 30, 508 (1934).

[12] F. A. Long and L. Friedman, J. Am. Chem. Soc. 72, 3692 (1950).

[13] J. Lander and I. N. Green, Trans. Far. Soc. 44, 408 (1948).

[14] C. A. Bunton, A. E. Comyns, and J. L. Wood, Res. 4, 383 (1951).

[15] N. I. Dedusenko and A. I. Brodsky, J. Gen. Chem. 12, 361 (1942).

[16] E. Blumenthal and I. B. M. Herbert, Trans. Far. Soc. 41, 611 (1945).

[17] A. I. Brodsky, Progr. Chem. 23, 614 (1954).

[18] A. H. V. Aten, Jr., J. Am. Chem. Soc. 74, 3706 (1952).

[19] D. I. Mendeleev, J. Russ. Chem. Soc. 2, 276 (1870); Ber. 3, 871 (1870).

[20] N. V. Sidgwick, The Chemical Elements and Their Compounds 2 (1950).

[21] A. I. Brodsky and R. K. Eremin, Proc. Acad. Sci. USSR 101, 487 (1955).

[22] K. K. Dubrovai and A. B. Sheinman, Oxidative Cracking, Moscow (1936).

[23] S. P. Obryadchikov, Petroleum Technology, Pt. II, Moscow, State Fuel Tech. Press (1952).

[24] L. Marek, Catalytic Oxidation of Organic Compounds, Moscow, United Sci.-Tech. Press (1936); A. M. Butlerov, Works, Vol. I, Moscow, Acad. Sci. USSR Press, p. 451 (1953); G. Charlot, Ann. Chim. 11, 415 (1934).

[25] N. N. Semenov, Some Problems of Chemical Kinetics and Reactivity, Moscow, Acad. Sci. USSR Press (1954).

[26] B. N. Dolgov, Catalysis in Organic Chemistry, Leningrad-Moscow, State Chem. Press (1948).

[27] A. N. Bakh, Collected Works on Chemistry and Biochemistry, Moscow, Acad. Sci. USSR Press (1950).

[28] V. Ya. Shtern and S. S. Polyak, Proc. Acad. Sci. USSR 84, 161 (1952); see also [71, 72].

[29] M. B. Neiman, A. F. Lukovnikov, and G. I. Feklisov, Questions of Chemical Kinetics, Catalysis, and Reactivity, Moscow, Acad. Sci. USSR Press, p. 184 (1955).

[30] P. V. Zimakov, Ethylene Oxide, Moscow-Leningrad, State. Chem. Press (1946).

[31] O. M. Todes and T. I. Andrianova, J. Chem. Phys. 27, 1483 (1953).

[32] A. Orzechowski and K. E. MacCormack, J. Canad. Chem. 32, 415, 443 (1954).

[33] G. H. Twigg, Proc. Roy. Soc. A188, 93 (1946).

[34] L. Ya. Margolis and S. Z. Roginsky, Proc. Acad. Sci. USSR 89, 515 (1953).

[35] L. Ya. Margolis and S. Z. Roginsky, Proc. Acad. Sci. USSR 96, 311 (1954).

[36] L. Ya. Margolis and S. Z. Roginsky, Proc. Acad. Sci. USSR 96, 549 (1954).

[37] L. Ya. Margolis and S. Z. Roginsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3, 281 (1956).

[38] G. I. Feklisov, Dissertation, Moscow Inst. Chem. Phys., Acad. Sci. USSR (1953); A. F. Lukovnikov and M. B. Neiman, Proc. Acad. Sci. USSR, 90, 583 (1953).

[39] R. Behrend, Ann. 333, 141 (1904).

[40] F. W. Klemperer, J. biol. Chem. 160, 111 (1945).

[41] W. Schuler and W. Reindel, Z. physiol. Chem. 208, 248 (1932).

[42] L. F. Cavalieri and G. B. Brown, J. Am. Chem. Soc. 70, 1242 (1948).

[43] L. F. Cavalieri, V. E. Blair, and G. B. Brown, J. Am. Chem. Soc. 70, 1240 (1948).

[44] B. Fries and M. Calvin, J. Am. Chem. Soc. 70, 2235 (1948).

[45] P. Nahinsky, C. Rice, S. Ruben, and M. D. Kamen, J. Am. Chem. Soc. 64, 2299 (1942).

[46] P. Nahinsky and S. Ruben, J. Am. Chem. Soc. 63, 2275 (1941).

[47] H. Taube and H. Dodgen, J. Am. Chem. Soc. 71, 3330 (1949).

[48] B. V. Klimenok, E. A. Andreev, O. V. Krylov, and M. M. Sakharov, Proc. Acad. Sci. USSR 95, 101 (1954).

[49] E. A. Andreev, T. I. Andrianova, B. V. Klimenok, O. V. Krylov, S. Z. Roginsky, and M. M. Sakharov, Proc. Acad. Sci. USSR 96, 781 (1954).

[50] M. M. Sakharov, Dissertation, Moscow, Inst. Phys. Chem., Acad. Sci. USSR (1955).

[51] G. N. Maslyansky and B. S. Berlin, J. Gen. Chem. 16, 1643 (1946).

[52] A. I. Brodsky, Isotope Chemistry, Moscow, Acad. Sci. USSR Press (1952).

[53] Wahl and Bonner (eds.), Radioactivity Applied to Chemistry, Moscow, Foreign Lit. Press (1954).

[54] Symposium, Isotopes in Microbiology, Moscow, Acad. Sci. USSR Press (1955).

[55] G. Hevesy, Radioactive Indicators, Moscow, Foreign Lit. Press (1950).

[56] E. Rabinowitch, Photosynthesis, Foreign Lit. Press, Moscow (1951).

[57] E. W. Steacie, Atomic and Free Radical Reactions, N. Y. (1954).

[58] J. Waersch, R. L. Huang, and K. Bloch, J. biol. Chem. 195, 439 (1952).

[59] D. J. Hanahan and S. I. Wakil, J. Am. Chem. Soc. 75, 273 (1953).

[60] F. V. Turchin, M. A. Guminskaya, and E. G. Plyshevskaya, Session of the Acad. Sci. USSR on the Peaceful Uses of Atomic Energy, July 1-5, 1955, Div. Biol. Sci., Moscow, Acad. Sci. USSR Press, p. 234 (1955).

[61] B. N. Stepanenko, Ibid., p. 305.

[62] A. I. Osipov, L. A. Shvartsman, V. E. Iudin, and M. L. Sazonov, Session of the Acad. Sci. USSR on the Peaceful Uses of Atomic Energy, July 1-5, 1955, Div. Tech. Sci., Moscow, Acad. Sci. USSR Press, p. 29 (1955); S. M. Gnuchev and V. G. Kuklev, Ibid. p. 69.

[63] I. M. Polyakov, Session of the Acad. Sci. USSR on the Peaceful Uses of Atomic Energy, July 1-5, 1955, Div. Tech. Sci., Moscow, Acad. Sci. USSR Press, p. 221 (1955); V. E. Pontovich, Ibid. p. 225.

[64] S. Ruben, M. Kamen, and W. Hassid, J. Am. Chem. Soc. 62, 3443 (1940).

[65] A. L. Kursanov, Problems of Botany, Coll. papers, I, Moscow, Acad. Sci. USSR Press (1954).

[66] O. V. Zalensky, O. A. Semikhatova, and V. L. Voznesensky, Methods of Using Radioactive Carbon C^{14} for the Study of Photosynthesis, Acad. Sci. USSR Press, Moscow (1954); O. V. Zalensky, Session of the Acad. Sci. USSR on the Peaceful Uses of Atomic Energy, July 1-5, 1955, Div. Biol. Sci., Moscow, Acad. Sci. USSR Press, p. 198 (1955).

[67] G. L. Gorodisskaya, M. B. Neiman, S. L. Rybakov, and R. B. Shnol, Proc. Acad. Sci. USSR 69, 833 (1949).

[68] M. B. Neiman, J. Phys. Chem. 28, 1235 (1954).

[69] M. B. Neiman and G. I. Feklisov, Proc. Acad. Sci. USSR 91, 1137 (1953).

[70] M. B. Neiman and G. I. Feklisov, J. Phys. Chem. 28, 1438, 1737 (1954).

[71] S. S. Polyak and V. Ya. Shtern, J. Phys. Chem. 27, 341 (1953).

[72] V. Ya. Shtern, Symposium, Questions of Chemical Kinetics, Catalysis, and Reactivity, Moscow, Acad. Sci. USSR Press, p. 197 (1950).

[73] M. B. Neiman and A. F. Lukovnikov, J. Phys. Chem. 29, 1410 (1955).

[74] I. N. Antonova, V. A. Kuzmin, R. I. Moshkina, A. B. Nalbandyan, M. B. Neiman, and G. I. Feklisov, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 789 (1955).

[75] L. A. Wall and W. J. Moore, J. Am. Chem. Soc. 73, 2840 (1951).

[76] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. 56, 284 (1934).

[77] F. O. Rice and K. K. Rice, The Aliphatic Free Radicals, USA (1935).

[78] V. V. Voevodsky, G. K. Lavrovskaya, and R. E. Mardaleishvili, Proc. Acad. Sci. USSR 81, 215 (1951).

[79] D. N. Kursanov and V. V. Voevodsky, Progr. Chem. 23, 641 (1954).

[80] I. E. Hobbs and C. N. Hinshelwood, Proc. Roy. Soc. A 167, 447 (1938).

[81] F. J. Stubbs and C. N. Hinshelwood, Proc. Roy. Soc. A 200, 458 (1950).

[82] F. O. Rice and R. E. Varnerin, J. Am. Chem. Soc. 76, 324 (1954).

[83] F. O. Rice and R. E. Varnerin, J. Am. Chem. Soc. 77, 221 (1955).

[84] C. D. Hurd and J. L. Azorlosa, J. Am. Chem. Soc. 73, 33 (1951).

[85] P. D. Zemany and M. Burton, J. Am. Chem. Soc. 73, 499 (1951).

[86] L. A. Wall and W. Moore, J. Phys. Coll. Chem. 55, 965 (1951).

[87] F. B. Blacet and R. K. Brinton, J. Am. Chem. Soc. 72, 4715 (1955).

[88] B. Gorin, Acta physicochim. URSS 8, 513 (1938); 9, 681 (1938); J. Chem. Phys. 7, 256 (1939).

[89] F. E. Blacet and I. D. Heldman, J. Am. Chem. Soc. 64, 889 (1942); F. E. Blacet and D. E. Loeffler, Ibid. 64, 893 (1942).

[90] M. H. J. Wijnen and E. W. R. Steacie, Canad. J. Chem. 29, 1092 (1951).

[91] K. J. Ivin and E. W. R. Steacie, Proc. Roy. Soc. A 208, 25 (1951).

[92] K. F. Bonhoeffer and P. Harteck, Z. phys. Chem. A 139, 263 (1928).

[93] H. von Wartenberg and G. Schultze, Z. phys. Chem. B2, 1 (1929).

[94] K. H. Geib and E. W. R. Steacie, Z. phys. Chem. B29, 215 (1935).

[95] G. K. Lavrovskaya, Dissertation, Moscow, Inst. Chem. Phys., Acad. Sci. USSR (1954); V. A. Poltorak and V. V. Voevodsky, Proc. Acad. Sci. USSR 91, 589 (1953).

[96] J. C. Bevington and H. W. Melville, Radioisotope Conference II, 3 (1954).

[97] L. Kaplan, J. Am. Chem. Soc. 76, 4645 (1954).

[98] L. Melander, Arkiv. Kemi 3, 525 (1952).

[99] J. Bigeleisen and M. Wolfsberg, J. Chem. Phys. 23, 1535 (1955).

[100] P. E. Yankwich and Alb. Promislow, J. Am. Chem. Soc. 76, 4648 (1954); P. E. Yankwich and R. Z. Belford, Ibid. 76, 3067 (1954).

[101] J. C. Polanyi, J. Chem. Phys. 23, 1505 (1955).

[102] D. R. Stranks, Trans. Far. Soc. 51, 505 (1955).

[103] D. R. Stranks, Ibid. 51, 515 (1955).

[104] E. S. Lewis and C. B. Boozer, J. Am. Chem. Soc. 76, 791 (1954).

[105] S. Yu. Elovich, S. Z. Roginsky, and E. I. Shmuk, Bull. Acad. Sci. USSR, Div. Chem. Sci. 469 (1950).

[106] E. I. Shmuk, Dissertation, Moscow, the M. V. Lomonosov Inst. Fine Chem. Technol. (1952).

[107] R. H. Griffith, The Mechanism of Contact Catalysis, Oxford (1946).

[108] G. K. Boreskov, Catalysis in Sulfuric Acid Manufacture, Moscow-Leningrad, State Chem. Press (1954).

[109] A. Mittasch and E. Theis, From Davy and Doebereiner to Deacon, Fifty Years of Heterogeneous Catalysis, Kharkov (1934).

[110] A. I. Khodnev, J. Min. Public Education No. 8, 75 (1852).

[111] S. M. Karpacheva and A. M. Rozen, Proc. Acad. Sci. USSR 68, 1057 (1949; 75, 239 (1950); 88, 507 (1953); J. Phys. Chem. 27, 146 (1953).

[112] F. M. Vainshtein and G. Ya. Turovsky, Proc. Acad. Sci. USSR 72, 297 (1950); 78, 1173 (1951); J. Phys. Chem. 28, 556 (1954).

[113] A. F. Benton, J. Am. Chem. Soc. 45, 887;900 (1923); Trans. Far. Soc. 28, 202 (1932).

[114] S. Z. Roginsky and Ya. B. Zeldovich, Acta physicochim. URSS 1, 595, 554 (1934).

[115] M. Katz, Advances in Catalysis 5, 177 (1953).

[116] V. N. Vasilyev, S. Yu. Elovich, and L. Ya. Margolis, Proc. Acad. Sci. USSR 101, 703 (1955).

[117] S. Yu. Elovich and F. F. Kharakhorin, Problems of Kinetics and Catalysis 3, 222 (1937).

[118] L. Ya. Margolis and S. Z. Roginsky, Summaries of Papers at the All-Union Conference on the Use of Isotopes in Catalysis, Acad. Sci. USSR Press, Moscow, p. 25 (1956).

[119] S. Z. Roginsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 17 (1940).

[120] N. N. Semenov and V. V. Voevodsky, Symposium, Heterogeneous Catalysis in Chemical Industry, Moscow, State Chem. Press, p. 233 (1955).

[121] F. F. Volkenshtein, Ibid., p. 213.

[122] A. E. Cahill and H. Taube, J. Am. Chem. Soc. 74, 2312 (1952).

[123] S. Z. Roginsky, Problems of Kinetics and Catalysis 8, 110 (1955).

[124] S. Z. Roginsky and O. V. Krylov, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 145 (1956).

[125] M. Bodenstein, Z. phys. Chem. 85, 329 (1913); Z. Elektrochem. 22, 53 (1916).

[126] J. A. Christiansen, J. phys. Chem. 28, 145 (1924); H. L. Bäckström, J. Am. Chem. Soc. 49, 1460 (1927); N. N. Semenov, Z. Phys. 46, 109 (1927); 48, 571 (1928); C. N. Hinshelwood and H. W. Thompson, Proc. Roy. Soc. 118, 170 (1927).

[127] M. V. Polyakov, Progr. Chem. 7, 351 (1948).

[128] M. A. Bogoyavlenskaya and A. A. Kovalsky, J. Phys. Chem. 20, 1325 (1946).

[129] P. Yu. Butyagin and S. Yu. Elovich, Proc. Acad. Sci. USSR 54, 60 (1946).

[130] V. V. Voevodsky, Problems of Kinetics and Catalysis 8, 97 (1955).

[131] E. I. Orlov, J. Russ. Phys.-Chem. Soc. 40, 1142, 1588 (1908).

[132] F. Fischer and H. Tropsch, Brennstoff-Chem. 7, 97 (1926); Ber. 59, 830, 923 (1926).

[133] V. A. Karzhavin, Progr. Chem. 16, 328 (1947); Ya. T. Eidus, Progr. Chem. 20, 54 (1951).

[134] H. Storch, N. Golumbic, and R. Anderson, The Fischer-Tropsch and Related Syntheses, Moscow, Foreign Lit. Press, pp. 480-500 (1954).

[135] J. T. Kummer, H. H. Podgurski, N. B. Spencer, and P. H. Emmett, J. Am. Chem. Soc. 73, 564 (1951), J. T. Kummer and P. H. Emmett, J. Am. Chem. Soc. 75, 5177 (1953).

[136] O. A. Golovina, S. Z. Roginsky, M. M. Sakharov, and T. Eidus, Proc. Acad. Sci. USSR 108, No. 3 (1956).

[137] R. S. Craxford and E. K. Rideal, J. Chem. Soc. 1604 (1939).

[138] Ya. T. Eidus and N. D. Zelinsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 289 (1940).

[139] Ya. T. Eidus, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 1, 65 (1943); No. 5, 355 (1944).

[140] V. V. Voevodsky, F. F. Volkenshtein, and N. N. Semenov, Symposium, Questions of Kinetics, Catalysis, and Reactivity, Moscow, Acad. Sci. USSR Press, p. 423 (1955).

[141] A. Farkas, L. Farkas, and E. K. Rideal, Proc. Roy. Soc. A 146, 630 (1934); A. Farkas, Trans. Far. Soc. 35, 906 (1939).

[142] E. Rideal and G. H. Twigg, Proc. Roy. Soc. A 171, 55 (1939).

[143] J. Horiuti and M. Polanyi, Trans. Far. Soc. 30, 1164 (1934); R. K. Greenhalgh, C. Horrex, and M. Polanyi, Trans. Far. Soc. 35, 511, 520 (1939).

[144] J. Douglas and B. Rabinowitch, J. Am. Chem. Soc. 74, 2486 (1952).

[145] B. M. W. Trapnell, Chemisorption, London, 1955; C. Kemball, Proc. Roy. Soc. A 223, 377 (1954); Trans. Far. Soc. 50, 1344 (1954).

[146] J. R. Anderson and C. Kemball, Proc. Roy. Soc. A 226, 472 (1954).

[147] D. D. Eley, Quart. Rev. Chem. Soc. 3, 209 (1949).

[148] G. J. Jenkins and E. Rideal, J. Chem. Soc. 2490, 2496 (1955).

[149] H. S. Taylor, J. Phys. Chem. 30, 145 (1926); Proc. Roy. Soc. A 108, 105 (1925); 12 Rep. Com. Cat. 41 (1940).

[150] D. P. Konovalov, J. Russ. Chem. Soc. 57, 383, 459 (1885).

[151] S. Z. Roginsky, Acta physicochim. URSS 4, 729 (1936); J. Phys. Chem. 15, 708 (1941).

[152] G. Hüttig, Nature 5, 9 (1935); G. F. Hüttig, Handbuch d. Katalyse, VI, 318-577, Wien, 1943.

[153] R. Fricke, Handbuch d. Katalyse, IV, 1 (1943).

[154] D. B. Dobychin, Problems of Kinetics and Catalysis 5, 165 (1948).

[155] V. L. Bonch-Bruevich and F. F. Volkenshtein, Problems of Kinetics and Catalysis 8, 218 (1955).

[156] G. M. Schwab and E. Pietsch, Z. Elektrochem. 35, 573 (1929).

[157] H. S. Taylor, Z. Elektrochem. 35, 542 (1929); H. S. Taylor and D. W. Jones, Progr. Chem. 3, 701 (1934).

[158] N. I. Kobozev, Symposium, Heterogeneous Catalysis in Chemical Industry, Moscow, State Chem. Press (1955).

[159] S. Z. Roginsky, J. Phys. Chem. 15, 1 (1941).

[160] S. Z. Roginsky, Bull. Acad. Sci. USSR, Phys. Ser. 4, No. 2, 350 (1940).

[161] F. Paneth and W. Vorwerk, Z. phys. Chem. 101, 445 (1922); F. Paneth, Radio-Elements as Indicators, London (1947).

[162] O. Hahn and O. Müller, Z. Elektrochem. 29, 189 (1923).

[163] N. E. Brezhneva and S. N. Oziraner, Scientific Research Work of the Chemical Institutes and Laboratories of the Academy of Sciences USSR in 1940, Collected Summaries, Acad. Sci. USSR Press (1941).

[164] G. M. Zhabrova, L. N. Kutseva, and S. Z. Roginsky, Proc. Acad. Sci. USSR 92, 569 (1952); 94, 73 (1954). G. M. Zhabrova, Progr. Chem. 24, 598 (1955).

[165] G. Hevesy and W. Seith, Z. Phys. 56, 790 (1929); Z. Electrochem. 37, 528 (1931); G. Hevesy and A. Obrutschewa, Nature 115, 674 (1925).

[166] A. N. Murin and B. G. Lurye, Proc. Acad. Sci. USSR 73, 933 (1950); 99, 53 (1954); A. N. Murin, G. N. Kazakova, and B. G. Lurye, Proc. Acad. Sci. USSR 99, 529 (1954).

[167] A. A. Zhukhovitsky, Session of the Acad. Sci. USSR on the Peaceful Uses of Atomic Energy, July 1-5, 1955, Div. Tech. Sci., Moscow, Acad. Sci. USSR Press, p. 101 (1955).

[168] A. N. Nesmeyanov, N. F. Lebedev, V. I. Lozgachev, and E. G. Chudinov, Session of the Acad. Sci. USSR on the Peaceful Uses of Atomic Energy, July 1-5, 1955, Div. Tech. Sci., Moscow, Acad. Sci. USSR Press, p. 79 (1955).

[169] O. Halin, Applied Radiochemistry, Moscow-Leningrad, State Chem. Press (1947).

[170] Radiography, Symposium, Moscow, Foreign Lit. Press (1952).

[171] M. Boudart, Ind. Eng. Chem. 46, 884 (1954).

[172] K. Hauffe, Z. angew. Chem. 67, 189 (1955).

[173] W. Shockley, Theory of Electronic Semiconductors, Moscow, Foreign Lit. Press (1953).

[174] W. Seitz, Diffusion in Metallen, Berlin, 1939.

[175] A. B. Shekhter and I. I. Tretyakov, Symposium, Heterogeneous Catalysis in Chemical Industry, Moscow, State Chem. Press, p. 349 (1955).

[176] P. A. Tesner and V. V. Keltsev, Carbon Black, Properties, Production, and Uses, Moscow-Leningrad, State Chem. Pres (1952).

[177] R. W. Blue and C. J. Engle, Ind. Eng. Chem. 43, 494 (1951).

[178] B. V. Kilmenok and A. B. Shekhter, Proc. Acad. Sci. USSR 83, 109 (1952).

[179] E. R. S. Winter, J. Chem. Soc. 3342 (1954); 2726 (1955).

[180] W. C. Cameron, A. Farkas, and L. Litz, J. Phys. Chem. 57, 229 (1953).

[181] L. A. Kasatkina, Dissertation, Moscow, D. I. Mendeleev Chem. Tech. Inst. (1953).

[182] G. P. McGeer and H. S. Taylor, J. Am. Chem. Soc. 73, 2743 (1951).

[183] A. D. Crowell and H. E. Farnsworth, J. Chem. Phys. 19, 1206 (1951); J. A. Dillon and H. E. Farnsworth, J. Chem. Phys. 22, 1601 (1954).

[184] E. M. Ioffe and B. A. Nikitin, Trans. Radium Inst. 6 (1955).

[185] B. P. Bering and V. V. Serpinsky, Problems of Kinetics and Catalysis 8, 243 (1955).

[186] T. N. Rhodin, Adv. in Catal. 5, 39 (1953).

[187] Jui Hsin Wang, Radioactivity Applied to Chemistry, Table IVA, p. 328, Moscow, Foreign Lit. Press (1954).

[188] L. S. Kolovrat-Chervinsky, Trans. Radium Expedition No. 9, Acad. Sci. USSR Press (1918).

[189] O. Hahn, J. Chem. Soc. (L.) 259 (1949).

[190] A. Wahl, Radioactivity Applied to Chemistry, Chapter 9, Moscow, Foreign Lit. Press (1954).

[191] H. Kaiser, Z. Elektrochem. 58, 601 (1954).

[192] C. Wagner, Z. phys. Chem. B21, 25 (1933); C. Wagner and K. Grünewald, Z. phys. Chem. B40, 455 (1938).

[193] K. Hauffe, Reaktionen in und an festen Stoffen, Berlin, p. 446 (1955).

[194] S. Z. Roginsky, I. I. Tretyakov, and A. B. Shekhter, Proc. Acad. Sci. USSR 91, 881, 1353 (1953); J. Phys. Chem. 29, No. 10, 1921 (1955).

[195] S. Z. Roginsky and E. I. Shults, Sci. Mem. Ekaterinoslav Sci.-Res. Inst., Dept. Chem. 190 (1926).

[196] Ya. B. Zeldovich and S. Z. Roginsky, Actaphysicochim. URSS 1, 57 (1934).

[197] S. Z. Roginsky, Nature 134, 935 (1934); Problems of Kinetics and Catalysis 3, 356 (1937).

[198] M. I. Temkin and V. I. Pyzhov, J. Phys. Chem. 13, 851 (1939).

[199] A. I. Shlygin and A. N. Frumkin, Proc. Acad. Sci. USSR 2, 176 (1934); A. N. Frumkin and A. I. Shlygin, Actaphysicochim. URSS 5, 819 (1936); J. Phys. Chem. 14, 1200 (1940).

[200] M. I. Temkin, J. Phys. Chem. 15, 296 (1941).

[201] S. Z. Roginsky, Adsorption and Catalysis on Heterogeneous Surfaces, Moscow, Acad. Sci. USSR Press (1948).

[202] L. Tonks, Phys. Rev. 50, 955 (1936); J. S. Wang, Proc. Roy. Soc. A 161, 127 (1937).

[203] I. Roberts, Some Problems in Adsorption, Cambridge, 1939; Proc. Cambr. Phil. Soc. 34, 577 (1938); 36, 53 (1940).

[204] N. I. Kobozev and Yu. B. Goldfeld, J. Phys. Chem. 10, 261 (1937).

[205] N. I. Kobozev and Yu. B. Goldfeld, J. Phys. Chem. 15, 257, 275 (1941).

[206] M. I. Temkin, J. Phys. Chem. 15, 314 (1941).

[207] I. Langmuir, Progr. Chem. 2, 649 (1933).

[208] F. F. Volkenshtein, J. Phys. Chem. 21, 163 (1947).

[209] F. F. Volkenshtein, J. Phys. Chem. 27, 159, 167 (1953); V. L. Bonch-Bruevich, J. Phys. Chem. 27, 663 (1953).

[210] P. B. Weisz, J. Chem. Phys. 20, 1483 (1952); 21, 1761; 1775 (1953).

[211] W. Schottky and F. Weibel, Naturwiss 20, 297 (1932); W. Schottky and W. Hartmann, Z. techn. Phys. 16, 512 (1935).

[212] M. Boudart, J. Am. Chem. Soc. 74, 3566 (1952).

[213] N. P. Keier and S. Z. Roginsky, Proc. Acad. Sci. USSR 57, 157 (1947).

[214] N. P. Keier, Symposium, Catalysts, p. 40, Kiev (1950).

[215] S. Z. Roginsky, Symposium, Heterogeneous Catalysis in Chemical Industry, Moscow, State Chem. Press, p. 29 (1955).

[216] N. P. Keier, Problems of Kinetics and Catalysis 8, 224 (1955).

[217] N. P. Keier and S. Z. Roginsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 27 (1950).

[218] P. H. Emmett and J. T. Kummer, J. Am. Chem. Soc. 73, 2886 (1951).

[219] L. N. Kurbatov, Author's Summary of Dissertation, Leningrad State Univ. (1954).

[220] N. P. Keier, Bull. Acad. Sci. USSR, Div. Chem. Sci. 616 (1952); 48 (1953).

[221] R. P. Eischens, J. Am. Chem. Soc. 74, 6167 (1952).

[222] G. P. Miklukhin, Dissertation, Inst. Phys. Chem., Acad. Sci. Ukrainian SSR (1954).

[223] G. P. Miklukhin and A. F. Rekasheva, Symposium, Questions of Chemical Kinetics, Catalysis, and Reactivity, Moscow, Acad. Sci. USSR Press, p. 24 (1955).

[224] I. P. Gragerov, Proc. Acad. Sci. USSR 99, 101 (1954); Symposium, Questions of Chemical Kinetics, Catalysis, and Reactivity, Moscow, Acad. Sci. USSR Press, p. 36 (1955).

[225] A. I. Brodsky, Session of the Acad. Sci. USSR on the Peaceful Uses of Atomic Energy, July 1-5, 1955, Div. Chem. Sci., Moscow, Acad. Sci. USSR Press, p. 210 (1955).

[226] F. Halverson, Rev. Mod. Phys. 19, 87 (1947).

[227] G. Herzberg, Spectra and Structure of Diatomic Molecules, Moscow, Foreign Lit. Press (1949); Infrared and Raman Spectra of Polyatomic Molecules, Moscow, Foreign Lit. Press (1949).

[228] M. V. Volkenshtein, Structure and Physical Properties of Molecules, Moscow, Acad. Sci. USSR Press (1955).

[229]* G. A. Razuvaev, G. G. Petrov, and N. A. Osanov, Proc. Acad. Sci. USSR 104, 733 (1955).

---

* In this investigation, in the decomposition of pentaphenylphosphorus molecules containing one deuterated phenyl group, removal occurred from equatorial and apical radicals with equal ease.

APPENDIX

I. TABLES OF THERMODYNAMIC FUNCTIONS

TABLE 1

Values of the Function $G = \frac{1}{2} - \frac{1}{u} + \frac{1}{e^u - 1}$ and its Relative Changes $\frac{\Delta G}{\Delta u}$ for Different Values of $u = \frac{hc\omega}{kT}$, After Bigeleisen and Mayer [1]

u	G	$\Delta G/\Delta u$	u	G	$\Delta G/\Delta u$
0.00	0.00000	—	1.75	0.13889	0.0722
0.05	0.004165	—	1.80	0.14247	0.0716
0.10	0.008415	—	1.85	0.14603	0.0712
0.15	0.01265	—	1.90	0.14955	0.0704
0.20	0.01671	—	1.95	0.15305	0.0700
0.25	0.02075	—	2.00	0.15652	0.0694
0.30	0.02496	—	2.05	0.15996	0.0688
0.35	0.02910	—	2.10	0.16335	0.0678
0.40	0.03326	0.0832	2.15	0.16672	0.0674
0.45	0.03738	0.0824	2.20	0.17006	0.0668
0.50	0.04150	0.0824	2.25	0.17337	0.0662
0.55	0.04561	0.0822	2.30	0.17665	0.0654
0.60	0.04970	0.0818	2.35	0.17989	0.0648
0.65	0.05379	0.0818	2.40	0.18310	0.0642
0.70	0.05787	0.0816	2.45	0.18628	0.0636
0.75	0.06193	0.0812	2.50	0.18943	0.0630
0.80	0.06597	0.0808	2.55	0.19253	0.0620
0.85	0.06999	0.0804	2.60	0.19561	0.0616
0.90	0.07401	0.0804	2.65	0.19866	0.0610
0.95	0.07800	0.0798	2.70	0.20168	0.0604
1.00	0.08198	0.0796	2.75	0.20465	0.0594
1.05	0.08593	0.0790	2.80	0.20761	0.0592
1.10	0.08987	0.0788	2.85	0.21051	0.0580
1.15	0.09378	0.0782	2.90	0.21339	0.0576
1.20	0.09768	0.0780	2.95	0.21625	0.0572
1.25	0.10155	0.0774	3.00	0.21906	0.0562
1.30	0.10540	0.0770	3.05	0.22184	0.0556
1.35	0.10922	0.0764	3.10	0.22459	0.0550
1.40	0.11302	0.0760	3.15	0.22731	0.0544
1.45	0.11680	0.0756	3.20	0.22999	0.0536
1.50	0.12055	0.0760	3.25	0.23264	0.0530
1.55	0.12428	0.0746	3.30	0.23526	0.0524
1.60	0.12797	0.0738	3.35	0.23785	0.0518
1.65	0.13164	0.0734	3.40	0.24041	0.0512
1.70	0.13528	0.0728			

TABLE 1 (continued)

u	G	ΔG/Δu	u	G	ΔG/Δu
3.45	0.24294	0.0506	5.65	0.32660	0.0280
3.50	0.24544	0.0500	5.70	0.32798	0.0276
3.55	0.24790	0.0492	5.75	0.32934	0.0272
3.60	0.25032	0.0484	5.80	0.33068	0.0268
3.65	0.25271	0.0478	5.85	0.33200	0.0264
3.70	0.25508	0.0474	5.90	0.33330	0.0260
3.75	0.25741	0.0466	5.95	0.33458	0.0256
3.80	0.25972	0.0462	6.00	0.33583	0.0250
3.85	0.26200	0.0456	6.10	0.33831	0.0252
3.90	0.26425	0.0450	6.20	0.34075	0.0244
3.95	0.26647	0.0444	6.30	0.34311	0.0236
4.00	0.26866	0.0438	6.40	0.34541	0.0230
4.05	0.27082	0.0432	6.50	0.34766	0.0225
4.10	0.27295	0.0426	6.60	0.34984	0.0218
4.15	0.27505	0.0420	6.70	0.35198	0.0214
4.20	0.27712	0.0414	6.80	0.35406	0.0208
4.25	0.27919	0.0408	6.90	0.35608	0.0202
4.30	0.28119	0.0402	7.00	0.35805	0.0197
4.35	0.28318	0.0398	7.10	0.35998	0.0193
4.40	0.28515	0.0394	7.20	0.36186	0.0188
4.45	0.28709	0.0388	7.30	0.36369	0.0183
4.50	0.28901	0.0384	7.40	0.36547	0.0178
4.55	0.29090	0.0378	7.50	0.36722	0.0175
4.60	0.29276	0.0372	7.60	0.36892	0.0170
4.65	0.29460	0.0368	7.70	0.37058	0.0166
4.70	0.29641	0.0362	7.80	0.37220	0.0162
4.75	0.29820	0.0358	7.90	0.37379	0.0159
4.80	0.29997	0.0354	8.00	0.37534	0.0155
4.85	0.30172	0.0350	8.10	0.37684	0.0150
4.90	0.30343	0.0342	8.20	0.37832	0.0148
4.95	0.30512	0.0338	8.30	0.37977	0.0145
5.00	0.30679	0.0334	8.40	0.38117	0.0140
5.05	0.30844	0.0330	8.50	0.38255	0.0138
5.10	0.31007	0.0326	8.60	0.38390	0.0135
5.15	0.31168	0.0322	8.70	0.38523	0.0133
5.20	0.31327	0.0318	8.80	0.38651	0.0128
5.25	0.31484	0.0314	8.90	0.38778	0.0127
5.30	0.31638	0.0308	9.00	0.38901	0.0123
5.35	0.31790	0.0304	9.10	0.39022	0.0121
5.40	0.31940	0.0300	9.20	0.39140	0.0118
5.45	0.32088	0.0296	9.30	0.39256	0.0116
5.50	0.32234	0.0292	9.40	0.39370	0.0114
5.55	0.32378	0.0288	9.50	0.39481	0.0111
5.60	0.32520	0.0284			

TABLE 1 (continued)

u	G	ΔG/Δu	u	G	ΔG/Δu
9.60	0.39590	0.0109	14.20	0.42958	0.0050
9.70	0.39697	0.0107	14.30	0.43007	0.0049
9.80	0.39802	0.0105	14.40	0.43056	0.0049
9.90	0.39904	0.0102	14.50	0.43103	0.0047
10.00	0.40005	0.0101	14.60	0.43151	0.0048
10.10	0.40103	0.0098	14.70	0.43197	0.0046
10.20	0.40200	0.0097	14.80	0.43243	0.0046
10.30	0.40294	0.0094	14.90	0.43289	0.0046
10.40	0.40388	0.0094	15.00	0.43333	0.0044
10.50	0.40479	0.0091	15.10	0.43377	0.0044
10.60	0.40568	0.0089	15.20	0.43421	0.0044
10.70	0.40656	0.0088	15.30	0.43464	0.0043
10.80	0.40743	0.0087	15.40	0.43506	0.0042
10.90	0.40828	0.0085	15.50	0.43548	0.0042
11.00	0.40911	0.0083	15.60	0.43590	0.0042
11.10	0.40993	0.0082	15.70	0.43631	0.0041
11.20	0.41072	0.0079	15.80	0.43671	0.0040
11.30	0.41151	0.0079	15.90	0.43711	0.0040
11.40	0.41229	0.0078	16.00	0.43750	0.0039
11.50	0.41305	0.0076	16.10	0.43789	0.0039
11.60	0.41380	0.0075	16.20	0.43827	0.0038
11.70	0.41454	0.0074	16.30	0.43865	0.0038
11.80	0.41526	0.0072	16.40	0.43902	0.0037
11.90	0.41598	0.0072	16.50	0.43939	0.0037
12.00	0.41668	0.0070	16.60	0.43976	0.0037
12.10	0.41736	0.0068	16.70	0.44012	0.0036
12.20	0.41803	0.0067	16.80	0.44048	0.0036
12.30	0.41870	0.0067	16.90	0.44083	0.0035
12.40	0.41935	0.0065	17.00	0.44118	0.0035
12.50	0.42000	0.0065	17.10	0.44152	0.0034
12.60	0.42063	0.0063	17.20	0.44186	0.0034
12.70	0.42126	0.0063	17.30	0.44220	0.0034
12.80	0.42187	0.0061	17.40	0.44253	0.0033
12.90	0.42248	0.0061	17.50	0.44286	0.0033
13.00	0.42308	0.0060	17.60	0.44318	0.0032
13.10	0.42366	0.0058	17.70	0.44350	0.0032
13.20	0.42424	0.0058	17.80	0.44382	0.0032
13.30	0.42481	0.0057	17.90	0.44413	0.0031
13.40	0.42537	0.0056	18.00	0.44444	0.0031
13.50	0.42593	0.0056	18.10	0.44475	0.0031
13.60	0.42647	0.0054	18.20	0.44505	0.0030
13.70	0.42701	0.0054	18.30	0.44536	0.0031
13.80	0.42754	0.0053	18.40	0.44565	0.0029
13.90	0.42806	0.0052	18.50	0.44595	0.0030
14.00	0.42857	0.0051	18.60	0.44624	0.0029
14.10	0.42908	0.0051			

TABLE 1 (continued)

u	G	ΔG/Δu	u	G	ΔG/Δu
18.70	0.44652	0.0028	21.70	0.45392	0.0022
18.80	0.44681	0.0029	21.80	0.45413	0.0021
18.90	0.44709	0.0028	21.90	0.45534	0.0021
19.00	0.44737	0.0028	22.00	0.45455	0.0021
19.10	0.44764	0.0027	22.10	0.45475	0.0020
19.20	0.44792	0.0028	22.20	0.45494	0.0020
19.30	0.44819	0.0027	22.30	0.45516	0.0021
19.40	0.44845	0.0026	22.40	0.45536	0.0020
19.50	0.44872	0.0027	22.50	0.45556	0.0020
19.60	0.44898	0.0026	22.60	0.45575	0.0019
19.70	0.44924	0.0026	22.70	0.45595	0.0020
19.80	0.44949	0.0025	22.80	0.45614	0.0019
19.90	0.44975	0.0026	22.90	0.45633	0.0019
20.00	0.45000	0.0025	23.00	0.45652	0.0019
20.10	0.45025	0.0025	23.10	0.45671	0.0019
20.20	0.45050	0.0025	23.20	0.45690	0.0019
20.30	0.45074	0.0024	23.30	0.45708	0.0018
20.40	0.45098	0.0024	23.40	0.45726	0.0018
20.50	0.45122	0.0024	23.50	0.45745	0.0019
20.60	0.45146	0.0024	23.60	0.45763	0.0018
20.70	0.45169	0.0023	23.70	0.45781	0.0018
20.80	0.45192	0.0023	23.80	0.45798	0.0017
20.90	0.45215	0.0023	23.90	0.45816	0.0018
21.00	0.45238	0.0023	24.00	0.45833	0.0017
21.10	0.45261	0.0023	24.10	0.45851	0.0018
21.20	0.45283	0.0022	24.20	0.45868	0.0017
21.30	0.45305	0.0022	24.30	0.45885	0.0017
21.40	0.45327	0.0022	24.40	0.45902	0.0017
21.50	0.45349	0.0022	24.50	0.45918	0.0016
21.60	0.45370	0.0021	24.60	0.45935	0.0017
			24.70	0.45951	0.0016
			24.80	0.45968	0.0017
			24.90	0.45984	0.0016
			25.00	0.46000	0.0016

TABLE 2

Functions for Calculation of the Influence of Isotopic Substitution on the Entropy S, Enthalpy H, and Heat Capacity C of an Ideal Gas, after Bigeleisen [2]

$$S(u_i) = \left[\frac{1}{u_i} - \frac{u_i e^{u_i}}{(e^{u_i}-1)^2}\right]$$

$$H(u_i) = \left[\frac{u_i e^{u_i}}{(e^{u_i}-1)^2} - \frac{1}{e^{u_i}-1}\right]$$

$$C(u_i) = \left[\frac{2\,u_i^2\,e^{2u_i}}{(e^{u_i}-1)^3} - \frac{u_i(u_i+2)\,e^{u_i}}{(e^{u_i}-1)^2}\right]$$

u	S(u)	ΔS/Δu	H(u)	ΔH/Δu	C(u)	ΔC/Δu
0.00	0.00000	0.0833	0.50000	0.1666	0.00000	0.1666
0.05	0.004166	0.0832	0.49167	0.1666	0.008331	0.1664
0.10	0.008329	0.0830	0.48334	0.1664	0.01665	0.1658
0.15	0.01248	0.0830	0.47502	0.1662	0.02494	0.1652
0.20	0.01663	0.0828	0.46671	0.1658	0.03320	0.1642
0.25	0.02077	0.0824	0.45842	0.1654	0.04141	0.1628
0.30	0.02489	0.0820	0.45015	0.1650	0.04955	0.1614
0.35	0.02899	0.0816	0.44190	0.1642	0.05762	0.1596
0.40	0.03307	0.0810	0.43369	0.1638	0.06560	0.1576
0.45	0.03712	0.0806	0.42550	0.1630	0.07348	0.1564
0.50	0.04115	0.0798	0.41735	0.1620	0.08125	0.1528
0.55	0.04514	0.0792	0.40925	0.1610	0.08889	0.1502
0.60	0.04910	0.0784	0.40120	0.1602	0.09640	0.1474
0.65	0.05302	0.0780	0.39319	0.1596	0.10377	0.1446
0.70	0.05692	0.0772	0.38521	0.1584	0.11100	0.1416
0.75	0.06078	0.0762	0.37729	0.1570	0.11808	0.1386
0.80	0.06459	0.0756	0.36944	0.1556	0.12501	0.1352
0.85	0.06835	0.0742	0.36166	0.1544	0.13177	0.1318
0.90	0.07206	0.0732	0.35394		0.13836	0.1282
0.95	0.07572	0.0726	0.34628	0.1532	0.14477	0.1242
1.00	0.07935	0.0706	0.33862		0.15098	0.1202
1.05	0.08288	0.0704	0.33119	0.1480	0.15699	0.1160
1.10	0.08640	0.0682	0.32376		0.16279	0.1100
1.15	0.08981	0.0676	0.31641	0.1463	0.16829	0.1050
1.20	0.09319	0.0664	0.30913		0.17354	0.1014
1.25	0.09651	0.0650	0.30194	0.1429	0.17861	0.0958
1.30	0.09976	0.0636	0.29484		0.18340	0.0938
1.35	0.10294	0.0624	0.28784	0.1393	0.18809	0.0878
1.40	0.10606	0.0612	0.28091		0.19248	0.0830
1.45	0.10912	0.0596	0.27408	0.1356	0.19663	0.0788
1.50	0.11210	0.0582	0.26735		0.20057	0.0734
1.55	0.11501	0.0568	0.26071	0.1318	0.20424	0.0688
1.60	0.11785	0.0556	0.25417		0.20768	0.0638
1.65	0.12063	0.0540	0.24773	0.1278	0.21087	0.0596
1.70	0.12333	0.0524	0.24139		0.21385	0.0544
1.75	0.12595	0.0510	0.23519	0.1237	0.21657	0.0494

TABLE 2 (continued)

u	$S(u)$	$\Delta S/\Delta u$	$H(u)$	$\Delta H/\Delta u$	$C(u)$	$\Delta C/\Delta u$
1.80	0.12850	0.0496	0.22902		0.21904	0.0450
1.85	0.13098	0.0482	0.22299	0.1196	0.22129	0.0406
1.90	0.13339	0.0464	0.21706		0.22332	0.0354
1.95	0.13571	0.0452	0.21123	0.1155	0.22509	0.0314
2.00	0.13797	0.0436	0.20551		0.22666	0.0266
2.05	0.14015	0.0422	0.19989	0.1112	0.22799	0.0226
2.10	0.14226	0.0406	0.19439		0.22912	0.0178
2.15	0.14429	0.0392	0.18900	0.1074	0.23001	0.0138
2.20	0.14625	0.0374	0.18365		0.23070	0.0090
2.25	0.14812	0.0362	0.17851	0.1023	0.23115	0.0060
2.30	0.14993	0.0348	0.17342		0.23145	0.0016
2.35	0.15167	0.0334	0.16844	0.0985	0.23153	—0.0018
2.40	0.15334	0.0316	0.16357		0.23144	0.0056
2.45	0.15492	0.0306	0.15880	0.0944	0.23116	0.0078
2.50	0.15644	0.0290	0.15413		0.23077	0.0148
2.55	0.15789	0.0278	0.14958	0.0902	0.23003	0.0162
2.60	0.15928	0.0260	0.14511		0.22922	0.0192
2.65	0.16058	0.0250	0.14076	0.0864	0.22826	0.0228
2.70	0.16183	0.0234	0.13647		0.22712	0.0256
2.75	0.16300	0.0222	0.13235	0.0821	0.22584	0.0286
2.80	0.16411	0.0210	0.12826		0.22441	0.0312
2.85	0.16516	0.0196	0.12433	0.0780	0.22285	0.0336
2.90	0.16614	0.0182	0.12046		0.22117	0.0362
2.95	0.16705	0.0172	0.11660	0.0743	0.21936	0.0386
3.00	0.16791	0.0160	0.11303		0.21743	0.0408
3.05	0.16871	0.0146	0.10946	0.0706	0.21539	0.0428
3.10	0.16944	0.0136	0.10597		0.21325	0.0450
3.15	0.17012	0.0124	0.10257	0.0670	0.21100	0.0466
3.20	0.17074	0.0112	0.09927		0.20867	0.0484
3.25	0.17130	0.0102	0.09606	0.0635	0.20625	0.0500
3.30	0.17181	0.0092	0.09292		0.20375	0.0516
3.35	0.17227	0.0082	0.08968	0.0601	0.20117	0.0530
3.40	0.17268	0.0070	0.08691		0.19852	0.0540
3.45	0.17303	0.0060	0.08403	0.0567	0.19582	0.0554
3.50	0.17333	0.0054	0.08124		0.19305	0.0560
3.55	0.17360	0.0042	0.07850	0.0536	0.19025	0.0574
3.60	0.17381	0.0034	0.07588		0.18738	0.0580
3.65	0.17398	0.0024	0.07332	0.0506	0.18448	0.0588
3.70	0.17410	0.0016	0.07082		0.18154	0.0596
3.75	0.17418	0.0008	0.06841	0.0476	0.17856	0.0598
3.80	0.17422	—0.0002	0.06606		0.17557	0.0604
3.85	0.17421	0.0008	0.06379	0.0448	0.17255	0.0608
3.90	0.17417	0.0016	0.06158		0.16951	0.0610
3.95	0.17409	0.0022	0.05944	0.0422	0.16646	0.0614
4.00	0.17398	0.0030	0.05736		0.16339	0.0614
4.05	0.17383	0.0038	0.05535	0.0395	0.16032	0.0614
4.10	0.17364	0.0042	0.05341		0.15725	0.0614

TABLE 2 (continued)

u	$S(u)$	$\Delta S/\Delta u$	$H(u)$	$\Delta H/\Delta u$	$C(u)$	$\Delta C/\Delta u$
4.15	0.17343	0.0048	0.05152	0.0372	0.15418	0.0614
4.20	0.17319	0.0058	0.04969		0.15111	0.0612
4.25	0.17290	0.0060	0.04791	0.0348	0.14805	0.0608
4.30	0.17260	0.0068	0.04621		0.14501	0.0608
4.35	0.17226	0.0072	0.04456	0.0327	0.14197	0.0606
4.40	0.17190	0.0078	0.04294		0.13894	0.0598
4.45	0.17151	0.0082	0.04140	0.0305	0.13595	0.0596
4.50	0.17110	0.0086	0.03989		0.13297	0.0590
4.55	0.17067	0.0092	0.03843	0.0286	0.13002	0.0586
4.60	0.17021	0.0096	0.03703		0.12709	0.0582
4.65	0.16973	0.0100	0.03567	0.0267	0.12418	0.0574
4.70	0.16923	0.0104	0.03436		0.12131	0.0570
4.75	0.16871	0.0108	0.03309	0.0250	0.11846	0.0562
4.80	0.16817	0.0110	0.03186		0.11565	0.0554
4.85	0.16762	0.0116	0.03066	0.0232	0.11288	0.0550
4.90	0.16704	0.0116	0.02954		0.11013	0.0540
4.95	0.16646	0.0122	0.02843	0.0218	0.10743	0.0534
5.00	0.16585	0.0124	0.02736		0.10476	0.0526
5.05	0.16523	0.0126	0.02633	0.0202	0.10213	0.0518
5.10	0.16460	0.0128	0.02534		0.09954	0.0508
5.15	0.16396	0.0130	0.02436	0.0188	0.09700	0.0502
5.20	0.16331	0.0134	0.02346		0.09449	0.0492
5.25	0.16264	0.0136	0.02253	0.0175	0.09203	0.0486
5.30	0.16196	0.0138	0.02171		0.08960	0.0476
5.35	0.16127	0.0138	0.02090	0.0164	0.08722	0.0466
5.40	0.16058	0.0142	0.02007		0.08489	0.0460
5.45	0.15987	0.0142	0.01925	0.0151	0.08259	0.0450
5.50	0.15916	0.0144	0.01856		0.08034	0.0442
5.55	0.15844	0.0146	0.01778	0.0141	0.07813	0.0432
5.60	0.15771	0.0146	0.01715		0.07597	0.0424
5.65	0.15698	0.0148	0.01642	0.0131	0.07385	0.0414
5.70	0.15624	0.0148	0.01584		0.07178	0.0408
5.75	0.15550	0.0150	0.01517	0.0121	0.06974	0.0398
5.80	0.15475	0.0150	0.01463		0.06775	0.0388
5.85	0.15400	0.0152	0.01401	0.0113	0.06581	0.0380
5.90	0.15324	0.0152	0.01350		0.06391	0.0372
5.95	0.15248	0.0152	0.01294	0.0104	0.06205	0.0362
6.00	0.15172	0.0153	0.01246		0.06024	0.0352
6.10	0.15019	0.0153	0.01150	0.0093	0.05672	0.0334
6.20	0.14866	0.0154	0.01060		0.05338	0.0318
6.30	0.14712	0.0154	0.00977	0.0079	0.05020	0.0303
6.40	0.14558	0.0154	0.00901		0.04717	0.0287
6.50	0.14404	0.0153	0.00730	0.0069	0.04430	0.0273
6.60	0.14251	0.0152	0.00764		0.04157	0.0258
6.70	0.14099	0.0152	0.00703	0.0058	0.03899	0.0244
6.80	0.13947	0.0151	0.00648		0.03655	0.0232
6.90	0.13796	0.0149	0.00596	0.0080	0.03423	0.0217

TABLE 2 (continued)

u	S(u)	ΔS/Δu	H(u)	ΔH/Δu	C(u)	ΔC/Δu
7.00	0.13647	0.0149	0.00548		0.03206	0.0207
7.10	0.13498	0.0147	0.00504	0.0042	0.02999	0.0194
7.20	0.13351	0.0146	0.00464		0.02805	0.0183
7.30	0.13205	0.0144	0.00426	0.0036	0.02622	0.0172
7.40	0.13061	0.0143	0.00392		0.02450	0.0163
7.50	0.12918	0.0141	0.00360	0.0031	0.02287	0.0152
7.60	0.12777	0.0139	0.00331		0.02135	0.0143
7.70	0.12638	0.0137	0.00304	0.0026	0.01992	0.0135
7.80	0.12501	0.0136	0.00279		0.01857	0.0126
7.90	0.12365	0.0134	0.00266	0.0022	0.01731	0.0118
8.00	0.12231	0.0131	0.00235		0.01613	0.0114
8.10	0.12100	0.0131	0.00220	0.0019	0.01499	0.0101
8.20	0.11969	0.0127	0.00198		0.01398	0.0097
8.30	0.11842	0.0126	0.00181	0.0016	0.01301	0.0091
8.40	0.11716	0.0124	0.00166		0.01210	0.0085
8.50	0.11592	0.0122	0.00153	0.0013	0.01125	0.0079
8.60	0.11470	0.0121	0.00140		0.01046	0.0074
8.70	0.11349	0.0118	0.00128	0.0011	0.00972	0.0069
8.80	0.11231	0.0116	0.00118		0.00903	0.0065
8.90	0.11115	0.0115	0.00107	0.0009	0.00838	0.0060
9.00	0.11000	0.0113	0.00099		0.00778	0.0056
9.10	0.10887	0.0110	0.00091	0.0008	0.00722	0.0052
9.20	0.10777	0.0109	0.00083		0.00670	0.0049
9.30	0.10668	0.0108	0.00076	0.0007	0.00621	0.0045
9.40	0.10560	0.0105	0.00070		0.00576	0.0042
9.50	0.10455	0.0103	0.00064	0.0006	0.00534	0.0040
9.60	0.10352	0.0102	0.00058		0.00494	0.0036
9.70	0.10250	0.0100	0.00053	0.0005	0.00458	0.0034
9.80	0.10150	0.0099	0.00049		0.00424	0.0032
9.90	0.10051	0.0096	0.00045	0.0004	0.00392	0.0029
10.00	0.09955	0.0095	0.00041		0.00363	0.0026
10.10	0.09860	0.0094	0.00038	0.0004		
10.20	0.09766	0.0092	0.00034		0.00311	0.0023
10.30	0.09674	0.0091	0.00032	0.0003		
10.40	0.09583	0.0088	0.00029		0.00266	0.0020
10.50	0.09495	0.0087	0.00026	0.0003		
10.60	0.09408	0.0086	0.00024		0.00227	0.0017
10.70	0.09322	0.0084	0.00022	0.0002		
10.80	0.09238	0.0084	0.00020		0.00194	0.0015
10.90	0.09154	0.0082	0.00018	0.0002		
11.00	0.09072	0.0080	0.00017		0.00165	0.0012
11.10	0.08992	0.0078	0.00015	0.0002		
11.20	0.08914	0.0078	0.00014		0.00141	0.0011
11.30	0.08836	0.0077	0.00013	0.0001		
11.40	0.08759	0.0075	0.00012		0.00120	0.0009
11.50	0.08684	0.0074	0.00011	0.0001		
11.60	0.08610	0.0073	0.00010		0.00102	

TABLE 2 (continued)

u	S(u)	ΔS/Δu	H(u)	ΔH/Δu	C(u)	ΔC/Δu
11.70	0.08537	0.0071	0.00009	0.0001		0.0008
11.80	0.08466	0.0071	0.00008		0.00087	
11.90	0.08395	0.0069	0.00007	0.0001		0.0007
12.00	0.08326	0.0068	0.00007		0.00074	
12.10	0.08258	0.0067	0.00006	0.0001		0.0006
12.20	0.08191	0.0067	0.00006		0.00063	
12.30	0.08124	0.0065	0.00006	0.0000		0.0005
12.40	0.08059	0.0064	0.00005		0.00053	
12.50	0.07995	0.0063	0.00005	0.0000		0.0004
12.60	0.07932	0.0062	0.00004		0.00045	
12.70	0.07870	0.0061	0.00004	0.0000		0.0004
12.80	0.07809	0.0060	0.00003		0.00038	
12.90	0.07749	0.0060				0.0003
13.00	0.07689	0.0058	0.00003		0.00032	
13.10	0.07631	0.0057				0.0003
13.20	0.07574	0.0057	0.00002		0.00027	
13.30	0.07517	0.0056				0.0002
13.40	0.07461	0.0055	0.00002		0.00023	
13.50	0.07406	0.0054				0.0002
13.60	0.07352	0.0054	0.00002		0.00020	
13.70	0.07298	0.0053				0.0002
13.80	0.07245	0.0052	0.00001		0.00016	
13.90	0.07193	0.0051				0.0001
14.00	0.07142	0.0051	0.00001		0.00014	
14.10	0.07091	0.0050				0.0001
14.20	0.07041	0.0049	0.00001		0.00012	
14.30	0.06992	0.0048				
14.40	0.06944	0.0048	0.00001		0.00010	
14.50	0.06896	0.0047				
14.60	0.06849	0.0047	0.00001		0.00008	
14.70	0.06802	0.0046				
14.80	0.06756	0.0045	0.00001		0.00007	
14.90	0.06711	0.0045				
15.00	0.06666	0.0044	0.00000		0.00006	
15.10	0.06622	0.0043				
15.20	0.06579	0.0043			0.00005	
15.30	0.06536	0.0043				
15.40	0.06493	0.0042			0.00004	
15.50	0.06451	0.0041				
15.60	0.06410	0.0041			0.00004	
15.70	0.06369	0.0040				
15.80	0.06329	0.0040			0.00003	
15.90	0.06289	0.0039				
16.00	0.06250	0.0039			0.00003	
16.10	0.06211	0.0038				
16.20	0.06173	0.0038			0.00002	
16.30	0.06135	0.0037				

TABLE 2 (end)

u	S(u)	ΔS/Δu	C(u)	u	S(u)	ΔS/Δu	C(u)
16.40	0 06098	0.0037	0.00002	20.70	0.04831	0.0023	
16.50	0 06061	0.0037		20.80	0.04808	0.0023	
16 60	0 06024	0.0036	0.00001	20.90	0.04785	0.0023	
16 70	0.05988	0.0036		21.00	0.04762	0.0023	
16.80	0 05952	0 0035	0.00001	21.10	0.04739	0.0022	
16 90	0 05917	0.0035		21.20	0.04717	0.0022	
17.00	0.05882	0.0034	0.00001	21.30	0.04695	0.0022	
17 10	0.05848	0.0034		21.40	0.04673	0.0022	
17 20	0 05814	0.0034	0.00001	21.50	0.04651	0.0022	
17 30	0.05780	0.0033		21.60	0.04629	0 0021	
17.40	0.05747	0.0033	0.00001	21.70	0.04608	0.0021	
17.50	0 05714	0.0032		21.80	0.04587	0.0021	
17 60	0.05682	0.0032	0.00001	21.90	0.04566	0.0021	
17.70	0 05650	0.0032		22.00	0.04545	0.0020	
17.80	0.05618	0.0031	0.00001	22.10	0.04525	0.0020	
17.90	0.05587	0 0031		22.20	0.04505	0.0021	
18 00	0.05556	0.0031	0 00000	22.30	0 04484	0.0020	
18.10	0.05525	0.0031		22.40	0.04464	0.0020	
18.20	0 05494	0 0030		22.50	0.04444	0.0020	
18.30	0.05464	0 0030		22.60	0.04424	0 0019	
18 40	0 05434	0.0029		22.70	0.04405	0 0019	
18 50	0.05405	0.0029		22.80	0.04386	0 0019	
18 60	0.05376	0.0028		22.90	0.04367	0.0019	
18 70	0 05348	0.0029		23.00	0.04348	0.0019	
18 80	0 05319	0.0028		23.10	0.04329	0.0019	
18.90	0.05291	0.0028		23.20	0.04310	0.0018	
19 00	0.05263	0 0028		23.30	0.04292	0.0018	
19 10	0.05235	0.0027		23.40	0.04274	0.0019	
19.20	0 05208	0.0027		23.50	0.04255	0.0018	
19 30	0.05181	0.0027		23.60	0.04237	0.0018	
19.40	0.05154	0.0026		23.70	0.04219	0.0018	
19 50	0.05128	0.0026		23.80	0 04201	0.0017	
19.60	0.05102	0.0026		23.90	0.04184	0.0017	
19.70	0.05076	0.0026		24.00	0.04167	0.0018	
19 80	0.05050	0.0025		24.10	0.04149	0.0017	
19 90	0.05025	0.0025		24.20	0.04132	0.0017	
20.00	0.05000	0.0025		24.30	0.04115	0.0017	
20 10	0.04975	0.0025		24.40	0.04098	0.0017	
20 20	0.04950	0.0024		24.50	0.04081	0.0016	
20.30	0.04926	0.0024		24.60	0.04065	0.0016	
20.40	0.04902	0.0024		24.70	0.04049	0.0017	
20.50	0 04878	0.0024		24.80	0.04032	0.0016	
20 60	0.04754	0 0023		24 90	0.04016	0.0016	
				25 00	0.04000		

TABLE 3

Molar Specific Heat Capacities C_p^0 of Isotopic Hydrogen Molecules, cal/degree · mole (for a normal ortho – para-mixture) [3]

T, °K	H_2	D_2	T_2	HD	HT	DT
3000	8.796	9.083	—	8.936	—	—
2500	8.531	8.879	9.011	8.687	8 758	8 943
2000	8.181	8.600	8.779	8 357	8.442	8.685
1750	7.963	—	—	—	—	—
1500	7.718	8.183	8.425	7.901	7 993	8 296
1250	7.457	7.893	8.166	7.619	7.708	8 021
1000	7.220	7.567	7.830	7.335	7.401	7.682
900	7.141	—	7.674	—	7.285	7 533
800	7.079	7.294	7.510	7.143	7 181	7 383
700	7.035	—	7.345	7.072	7.096	7.243
600	7.008	7.081	7.106	7.025	7.037	7.124
500	6.992	7.019	7.077	6.998	7 002	7 039
400	6.974	6.985	7.007	6.985	6.986	6 994
350	6.950	—	—	—	—	—
300	6.896	6.977	6.978	6 978	6.978	6 977
298.1	6.895	6.977	6 978	6.978	6 978	6 977
275	6.848	6.976	6.975	6.997	6.976	6.975
250	6 772	6.975	6.973	6 976	6 975	6 973
225	—	—	—	—	—	6.972
200	6.525	6.978	6.969	6.974	6.973	6.970
175	—	—	—	—	—	6 969
150	6.077	7.030	6.963	6.977	6 974	6.968
125	5.751	7.104	6.945	6.983	6.977	6 968
100	5.401	7.192	6.874	6 998	6.987	6 969
75	5.105	7.022	6.664	7 055	7 023	6.975
50	4.980	5.691	6.091	7.149	7 141	7 010
40	4 971	5.410	5.653	6 996	7.110	7.064
30	4.970	5 061	5.247	6 376	6 676	7 147
25	4.970	4.992	5.087	5.872	6 195	7 106
20	4.970	4.970	5.001	5.371	5 607	6 806
15	4.970	4.970	4 971	5.053	5 142	6 065
10	—	4.970	4.967	4.970	4 977	5 203
0	0.000	0.000	0 000	0 000	0 000	0.000

TABLE 3a

Enthalpies $H_T^0 - E_0$ of Isotopic Hydrogen Molecules, cal/mole (for normal ortho—para-mixtures of H_2, D_2, T_2)

T, °K	H_2	D_2	T_2	HD	HT	DT*
3000	23196	23196	—	23560	—	—
2500	18862	19605	20026	19250	19299	19717
2000	14680	15235	15576	14880	14996	15386
1750	12647	13100	13382	12807	12905	—
1500	10699	11030	11267	10810	10880	11134
1300	9177	—	—	—	—	—
1250	8800	9020	9192	8874	8916	9094
1000	6968	7085	7191	7043	7028	7129
900	6249	6335	6415	6280	6294	6367
800	5528	5600	5656	5559	5570	5622
700	4832	4876	4913	4850	4857	4891
600	4129	4164	4186	4145	4147	4173
500	3430	3459	3473	3443	3448	3465
400	2731	2759	2769	2745	2749	2764
300	2036	2061	2070	2040	2051	2065
298 16	2024	2047	2057	2033	2038	2032
275	1864	1886	1896	1872	1877	1891
250	1649	1712	1722	1698	1702	1717
200	1361	1363	1373	1349	1354	1368
175	1200	1189	1109	1158	1179	1194
150	1045	1013	1025	978	1005	1020
125	897	836	851	809	831	846
100	759	658	678	654	656	671
75	626.9	479 2	507.2	477.5	481.1	497.1
50	501.3	315.0	348.9	297.7	304.2	322.4
25	377.1	181.0	210.1	128.7	131.1	145.3
10	302.6	106.6	135.1	46.6	49.7	50.0
0	252.9	56.7	85 5	0.0	0.0	0.0

* and. T, °K — 225	40	30	20	15
$H_0 - E_0$ — 1543	252.1	181.0	110.4	78.0

TABLE 3b.

Values of the Function $\left(\frac{\Phi^0 - E_0^0}{T}\right)$ cal/mole, for Isotopic Hydrogen Molecules (for normal ortho—para-mixtures of H_2, D_2, T_2)*

T, °K	H_2	D_2	T_2	HD	HT	DT
3000	40 739	44.417	—	43 973	—	—
2500	39.346	42.970	45.137	42.559	43.685	45.438
2000	37.686	41.245	43 375	40 875	41.990	43.697
1500	35.606	39.094	41.174	38 769	39 869	41.524
1250	34.315	37.766	39 818	37.405	38.598	40 184
1000	32.753	36.171	38 198	35.855	36 979	38.579
900	32.021	35.427	37.443	35.155	36.240	37 830
800	31.205	34.600	36.607	34 335	35.418	36 999
700	30.281	33 668	35.666	33.408	34.491	36.064
600	29.219	32.596	34.587	32 342	33.422	34.989
500	27.966	31.333	33.319	31.085	32 164	33.724
400	26.439	29.792	31.771	29.550	30 627	32.179
300	24.481	27.811	29.783	27.577	28 054	30 195
298.1	24.437	27.768	29.739	27.539	28 611	30 152
275	23.949	27.231	29.183	26.977	28 060	29 596
250	23.246	26.561	28.526	26.341	27 410	28.942
225	22.530	25 841	27.831	—	26.694	28 218
200	21.730	25.035	26.991	24 831	25 895	27.411
175	20.818	24.128	26.076	24.031	24.993	26.499
150	19.752	23.082	25.021	23 042	23.957	25 449
125	18.468	21 871	23.778	21.857	22.740	24 213
100	16.818	20.374	22.262	20.228	21 267	22 709
75	14.528	18.466	20.283	18 410	19.399	20.789
50	10.818	16.032	17.534	15.879	16 859	18 135
25	2.294	11.380	12.302	12.053	12.935	13 854
10	—17.496	3.362	2.618	—	8 321	8 990
0	—∞	—∞	—∞	0.000	0 000	—

---

* Φ_g is the Gibbs free energy. In Zeise's papers it is denoted by G.

TABLE 3c

Entropies S^0 of Isotopic Hydrogen Molecules, cal/degree·mole (for normal ortho–para-mixtures of H_2, D_2, T_2)

T, °K	H_2	D_2	T_2	HD	HT	DT
3000	48 471	52 449	—	51.826	—	—
2750	47.712	—	—	—	—	—
2500	46.891	50 812	53.147	50 220	51.405	53.357
2250	45 999	—	—	—	—	—
2000	45 026	48 862	51 162	48.317	49.488	51.390
1750	43 948	47.733	50.006	47.229	48.380	—
1500	42.739	46 448	48.686	45.977	47.123	48.947
1400	42 210	45.885	48.102	45 443	46.570	—
1300	41.649	45.287	47.480	44.861	45.982	—
1250	41.412	44.984	47.172	44 564	45.691	47.459
1200	41.053	44.652	46.821	44.242	45.358	—
1100	40.412	43.976	46 123	43.588	44 699	—
1000	39.721	43 256	45.387	42.898	44.006	45.708
900	38.964	42.460	44 571	42.433	43.233	44.905
800	38 115	41.600	43.676	41.284	42.382	44.027
700	37.184	40.634	42.685	40.336	41.429	43.051
600	36 101	39 536	41.565	39 250	40.340	41.944
500	34.826	38 251	40.265	37.972	39.061	40.655
400	33 267	36.689	38.695	36 412	37.500	39.089
300	31.269	34.680	36.684	34.398	35.492	37.080
298 1	31.23	34 636	36.040	34.394	35.448	37.037
275	30.669	34 090	36.077	33.784	34.885	36.473
250	30 022	33.409	35.412	33.131	34.220	35.809
225	29.312	32.674	34 678	32.400	33.485	35.074
200	28.535	31.850	33.857	31.575	32.664	34.253
175	27.677	30.922	32.696	30.648	31.733	33.323
150	26.720	29.838	31.853	29.563	30.658	32.248
125	25.641	28.559	30.584	28.329	29.386	30.978
100	24.406	26.955	29.041	26.736	27.828	29 423
75	22.880	24.855	27.076	24 777	25.814	27.417
50	20.844	22.332	24.514	21.833	22.944	24.584
40	—	—	—	—	—	23.014
30	—	—	—	—	—	20.969
25	17.341	18.570	20 706	17.201	18.180	19.667
20	—	—	—	—	—	18.109
15	—	—	—	—	—	16.252
10	12.759	14.022	16.132	—	13.289	13.991
0	1.638	0.728	1.638	0 000	0.000	—

TABLE 4

Thermodynamic Functions of Different Isotopic Forms of Water, Calculated for an Ideal Gas Model [4].

$$\frac{C_p^0}{R} = \frac{Q''}{QT^2} - \left(\frac{Q'}{QT}\right)^2$$

$$\frac{(H^0 - E_0^0)}{RT} = -\left(\frac{Q'}{QT}\right)$$

$$\left(\frac{\Phi^0 - E_0^0}{RT}\right) = -\ln Q$$

$$\frac{S^0}{R} = -\left(\frac{Q'}{QT}\right) + \ln Q$$

$$Q = Q_T\left[\prod_i (1 - e^{u_i})^{-1}\right] \cdot \frac{1}{S}\left[\frac{\pi}{\sigma_{A_e}\sigma_{B_e}\sigma_{C_e}}\right]^{1/2} \cdot \left[1 + \frac{Q_1}{T} + \frac{Q_2}{T^2}\right] \times$$

$$\times [1 + \rho T]\left[\prod_{i<j}(1 + f_{ij})\right] \cdot \left[\prod_i\left(1 + \frac{1}{2}\,\frac{\delta_i}{2(e^{u_i} - 1)}\right)\right]$$

TABLE 4a

Principal Molecular Constants Used for Calculations of the Thermodynamic Functions

Constant	H_2O	HDO	D_2O	HTO	DTO	T_2O
ν_1 cm^{-1}	3657.05	2723.66	2671.69	2295	2290	2233
ν_2 cm^{-1}	1594.59	1402.80	1178.33	1343	1097	998
ν_3 cm^{-1}	3755.79	3707.47	2788.02	3703	2733	2365
X_{11} cm^{-1}	42.566	43.39	21 88	30.4	30.2	15 3
X_{22} cm^{-1}	16 813	10.12	9 42	9.22	6 09	6.41
X_{33} cm^{-1}	47.560	82.58	26.30	82.4	43 8	18.2
X_{12} cm^{-1}	15.933	8.50	8.77	6.76	5.48	5.88
X_{13} cm^{-1}	165.824	12.99	85.73	11 1	8 09	61 6
X_{23} cm^{-1}	20.332	20.68	10 17	19 6	11 6	7 75
δ_1	0.063	0.047	0.044	0.039	0 039	0 038
δ_2	−0.1016	−0.082	−0.070	−0.077	−0.063	−0.062
δ_3	+0.0648	+0.062	+0.051	+0.062	+0 045	+0.040
I_e^A g·cm^2·10^{40}	1.0224	1.211	1.833	1 250	2 068	2 502
I_e^B g·cm^2·10^{40}	1.9180	3.060	3.841	4.225	4 861	5 742
I_e^C g·cm^2·10^{40}	2.9404	4.271	5.674	5 475	6 928	8 244
θ_1, °K	4.448	3.076	2 326	2 406	1 823	1 606
θ_2, °K	19.39	9.13	5.13	5 57	3.16	2 43
ρ(°K)$^{-1}$·10^5	2.13	2.13	2.13	2 13	2 13	2 13

TABLE 4b

T,°K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
50	4.00719	3.90579	11.63213	15.53793
60	4.00634	3.92262	12.34582	16.26844
70	4.00590	3.93454	12.95144	16.88599
80	4.00573	3.94345	13.47744	17.42089
90	4.00571	3.95037	13.94232	17.89260
100	4.00581	3.95591	14.35883	18.31474
110	4.00599	3.96045	14.73609	18.69655
120	4.00622	3.96425	15.08086	19.04512
130	4.00649	3.96749	15.39830	19.30580
140	4.00680	3.97029	15.69243	19.66273
150	4.00715	3.97273	15.96644	19.93918
160	4.00755	3.97490	16.22290	20.19781
170	4.00803	3.97683	16.46394	20.44078
180	4.00860	3.97858	16.69130	20.66989
190	4.00931	3.98018	16.90646	20.88664
200	4.01020	3.98166	17.11065	21.09231
210	4.01132	3.98304	17.30495	21.28800
220	4.01272	3.98436	17.49027	21.47463
230	4.01446	3.98563	17.66741	21.65304
240	4.01658	3.98687	17.83706	21.82394
250	4.01912	3.98811	17.99984	21.98796
260	4.02214	3.98936	18.15628	22.14565
270	4.02565	3.99063	18.30687	22.29751
280	4.02970	3.99196	18.45202	22.44398
290	4.03428	3.99334	18.59213	22.58547
300	4.03942	3.99478	18.72753	22.72232
310	4.04511	3.99631	18.85855	22.85486
320	4.05136	3.99794	18.98545	22.98339
330	4.05815	3.99966	19.10850	23.10816
340	4.06547	4.00148	19.22793	23.22941
350	4.07329	4.00342	19.34395	23.34737
360	4.08160	4.00548	19.45676	23.46224
370	4.09038	4.00765	19.56653	23.57419
380	4.09958	4.00995	19.67344	23.68339
390	4.10920	4.01237	19.77763	23.79000
400	4.11919	4.01491	19.87925	23.89417
450	4.17394	4.02948	20.35295	24.38243
500	4.23453	4.04691	20.77837	24.82529
550	4.29891	4.06687	21.16500	25.23188
600	4.36590	4.08898	21.51980	25.60879
650	4.43498	4.11293	21.84803	25.96097
700	4.50589	4.13846	22.15376	26.29222
750	4.57847	4.16536	22.44019	26.60556
800	4.65252	4.19349	22.70991	26.90340
850	4.72770	4.22270	22.96501	27.18771

TABLE 4b (end)

T,°K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
900	4.80384	4.25287	23.20722	27.46010
950	4.88035	4.28388	23.43799	27.72188
1000	4.95688	4.31562	23.65853	27.97415
1050	5.03302	4.34797	23.86987	28.21784
1100	5.10838	4.38082	24.07289	28.45372
1150	5.18263	4.41407	24.26836	28.68244
1200	5.25547	4.44762	24.45693	28.90456
1300	5.39600	4.51521	24.81560	29.33082
1400	5.52862	4.58291	25.15269	29.73561
1500	5.65262	4.65014	25.47118	30.12132
1600	5.76780	4.71644	25.77341	30.48986
1700	5.87429	4.78146	26.06130	30.84277
1800	5.97247	4.84494	26.33641	31.18135
1900	6.06284	4.90669	26.60002	31.50672
2000	6.14596	4.96661	26.85324	31.81985
2100	6.22241	5.02461	27.09697	32.12159
2200	6.29278	5.08068	27.33202	32.41270
2300	6.35761	5.13481	27.55906	32.69388
2400	6.41741	5.18702	27.77871	32.96573
2500	6.47267	5.23736	27.99148	33.22884
2600	6.52381	5.28586	28.19784	33.48371
2700	6.57122	5.33260	28.39822	33.73082
2800	6.61527	5.37764	28.59207	33.97061
2900	6.65625	5.42103	28.78244	34.20347
3000	6.69447	5.46285	28.96693	34.42978
3200	6.76361	5.54203	29.32205	34.86409
3400	6.82440	5.61571	29.66027	35.27599
3600	6.87824	5.68439	29.98323	35.66762
3800	6.92626	5.74851	30.29230	36.04082
4000	6.96936	5.80849	30.58871	36.39720
4200	7.00826	5.86471	30.87348	36.73820
4400	7.04358	5.91751	31.14754	37.06505
4600	7.07580	5.96718	31.41169	37.37887
4800	7.10532	6.01400	31.66665	37.68065
5000	7.13248	6.05820	31.91306	37.97126

TABLE 4c

T,°K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
50	4.00480	3.93645	12.88338	16.81984
60	4.00450	3.94781	13.60215	17.54997
70	4.00446	3.95591	14.21135	18.16726
80	4.00456	3.96198	14.74000	18.70199
90	4.00476	3.96672	15.20694	19.17367
100	4.00501	3.97054	15.62508	19.59562
110	4.00531	3.97368	16.00367	19.97736
120	4.00565	3 97633	16.34954	20.32588
130	4.00602	3.97860	16.66791	20.64652
140	4 00645	3.98058	16.96283	20.94341
150	4.00696	3.98232	17.23752	21.21985
160	4 00760	3.98388	17.49459	21.47847
170	4.00843	3.98530	17.73615	21.72145
180	4.00951	3.98661	17.96398	21.95060
190	4.01091	3.98785	18.17956	22.16742
200	4.01273	3.98905	18.38414	22.37349
210	4.01502	3.99023	18.57880	22.56903
220	4.01786	3.99142	18.76445	22.75587
230	4.02132	3.99264	18.94190	22.93455
240	4.02544	3.99392	19.11185	23.10578
250	4.03026	3.99527	19.27492	23.27020
260	4.03580	3.99672	19.43165	23.42837
270	4.04208	3.99828	19.58251	23.58080
280	4.04909	3.99997	19.72795	23.72793
290	4.05683	4.00180	19.86835	23.87015
300	4.06529	4.00377	20.00405	24.00782
310	4.07443	4.00590	20.13536	24.14127
320	4.08423	4.00819	20.26258	24.27078
330	4.09465	4.01065	20.38596	24.39662
340	4.10566	4.01328	20.50573	24.51902
350	4.11723	4.01609	20.62210	24.63820
360	4.12932	4.01906	20.73528	24.75435
370	4.14188	4.02221	20.84544	24.86766
380	4.15489	0.02553	20.95275	24.97829
390	4.16831	4.02902	21.05736	25.08639
400	4.18211	4.03267	21.15941	25.19209
450	4.25578	4.05331	21.63555	25.68886
500	4.33522	4.07749	22.06383	26.14132
550	4.41850	4.10468	22.45371	26.55839
600	4.50444	4.13440	22.81212	26.94652
650	4.59218	4.16623	23.14429	27.31052
700	4.68108	4.19982	23.45426	27.65409
750	4.77049	4.23488	23.74521	27.98010
800	4.85983	4.27115	24.01968	28.29083
850	4.94855	4.30840	24.27973	28.58813

TABLE 4b (end)

T,°K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
900	4.80384	4.25287	23.20722	27.46010
950	4.88035	4.28388	23.43799	27.72188
1000	4.95688	4.31562	23.65853	27 97415
1050	5.03302	4.34797	23.86987	28.21784
1100	5.10838	4.38082	24.07289	28 45372
1150	5.18263	4.41407	24.26836	28.68244
1200	5.25547	4.44762	24.45693	28.90456
1300	5.39600	4.51521	24.81560	29.33082
1400	5.52862	4.58291	25.15269	29.73561
1500	5.65262	4.65014	25.47118	30.12132
1600	5.76780	4.71644	25.77341	30.48986
1700	5.87429	4.78146	26.06130	30.84277
1800	5.97247	4.84494	26.33641	31.18135
1900	6.06284	4.90669	26.60002	31.50672
2000	6.14596	4.96661	26.85324	31.81985
2100	6.22241	5.02461	27.09697	32.12159
2200	6.29278	5.08068	27.33202	32 41270
2300	6.35761	5.13481	27.55906	32.69388
2400	6.41741	5.18702	27.77871	32.96573
2500	6.47267	5.23736	27 99148	33.22884
2600	6.52381	5.28586	28.19784	33.48371
2700	6.57122	5.33260	28.39822	33.73082
2800	6.61527	5 37764	28.59297	33.97061
2900	6.65625	5.42103	28.78244	34.20347
3000	6.69447	5.46285	28.96693	34.42978
3200	6.76361	5.54203	29.32205	34.86409
3400	6.82440	5.61571	29.66027	35.27509
3600	6.87824	5.68439	29.98323	35.66762
3800	6.92626	5.74851	30.29230	36.04082
4000	6.96936	5.80849	30.58871	36.39720
4200	7.00826	5.86471	30.87348	36 73820
4400	7.04358	5.91751	31.14754	37 06505
4600	7.07580	5.96718	31.41169	37.37887
4800	7.10532	6.01400	31.66665	37.68065
5000	7.13248	6.05820	31.91306	37.97126

TABLE 4c

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
50	4.00480	3.93645	12.88338	16.81984
60	4.00450	3.94781	13.60215	17.54997
70	4.00446	3.95591	14.21135	18.16726
80	4.00456	3.96198	14.74000	18.70199
90	4.00476	3.96672	15.20694	19.17367
100	4.00501	3.97054	15.62508	19.59562
110	4.00531	3.97368	16.00367	19.97736
120	4.00565	3.97633	16.34954	20.32588
130	4.00602	3.97860	16.66791	20.64652
140	4.00645	3.98058	16.96283	20.94341
150	4.00696	3.98232	17.23752	21.21985
160	4.00760	3.98388	17.49459	21.47847
170	4.00843	3.98530	17.73615	21.72145
180	4.00951	3.98661	17.96398	21.95060
190	4.01091	3.98785	18.17956	22.16742
200	4.01273	3.98905	18.38414	22.37319
210	4.01502	3.99023	18.57880	22.56903
220	4.01786	3.99142	18.76445	22.75587
230	4.02132	3.99264	18.94190	22.93455
240	4.02544	3.99392	19.11185	23.10578
250	4.03026	3.99527	19.27492	23.27020
260	4.03580	3.99672	19.43165	23.42837
270	4.04208	3.99828	19.58251	23.58080
280	4.04909	3.99997	19.72795	23.72793
290	4.05683	4.00180	19.86835	23.87015
300	4.06529	4.00377	20.00405	24.00782
310	4.07443	4.00590	20.13536	24.14127
320	4.08423	4.00819	20.26258	24.27078
330	4.09465	4.01065	20.38596	24.39662
340	4.10566	4.01328	20.50573	24.51902
350	4.11723	4.01609	20.62210	24.63820
360	4.12932	4.01906	20.73528	24.75435
370	4.44188	4.02221	20.84544	24.86766
380	4.15489	0.02553	20.95275	24.97829
390	4.16831	4.02902	21.05736	25.08639
400	4.18211	4.03267	21.15941	25.19209
450	4.25578	4.05331	21.63555	25.68886
500	4.33522	4.07749	22.06383	26.14132
550	4.41850	4.10468	22.45371	26.55839
600	4.50444	4.13440	22.81212	26.94652
650	4.59218	4.16623	23.14429	27.31052
700	4.68108	4.19982	23.45426	27.65409
750	4.77049	4.23488	23.74521	27.98010
800	4.85983	4.27115	24.01968	28.29083
850	4.94855	4.30840	24.27973	28.58813

TABLE 4.b (end)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
900	4.80384	4.25287	23.20722	27.46010
950	4.88035	4.28388	23.43799	27.72188
1000	4.95688	4.34562	23.65853	27.97415
1050	5.03302	4.34797	23.86987	28.21784
1100	5.10838	4.38082	24.07289	28.45372
1150	5.18263	4.41407	24.26836	28.68244
1200	5.25547	4.44762	24.45693	28.90456
1300	5.39600	4.51521	24.81560	29.33082
1400	5.52862	4.58291	25.15269	29.73561
1500	5.65262	4.65014	25.47118	30.12132
1600	5.76780	4.71644	25.77341	30.48986
1700	5.87429	4.78146	26.06130	30.84277
1800	5.97247	4.84494	26.33641	31.18135
1900	6.06284	4.90669	26.60002	31.50672
2000	6.14596	4.96661	26.85324	31.81985
2100	6.22241	5.02461	27.09697	32.12159
2200	6.29278	5.08068	27.33202	32.41270
2300	6.35761	5.13481	27.55906	32.69388
2400	6.41741	5.18702	27.77871	32.96573
2500	6.47267	5.23736	27.99148	33.22884
2600	0.52381	5.28586	28.19784	33.48371
2700	6.57122	5.33260	28.39822	33.73082
2800	6.61527	5.37764	28.59297	33.97061
2900	6.65625	5.42103	28.78244	34.20347
3000	6.69447	5.46285	28.96693	34.42978
3200	6.76361	5.54203	29.32205	34.86409
3400	6.82440	5.61571	29.66027	35.27599
3600	6.87824	5.68439	29.98323	35.66762
3800	6.92626	5.74851	30.29230	36.04082
4000	6.96936	5.80849	30.58871	36.39720
4200	7.00826	5.86471	30.87348	36.73820
4400	7.04358	5.91751	31.14754	37.06505
4600	7.07580	5.96718	31.41169	37.37887
4800	7.10532	6.01400	31.66665	37.68065
5000	7.13248	6.05820	31.91306	37.97126

TABLE 4c

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
50	4.00480	3.93645	12.88338	16.81984
60	4.00450	3.94781	13.60215	17.54997
70	4.00446	3.95591	14.21135	18.16726
80	4.00456	3.96198	14.74000	18.70199
90	4.00476	3.96672	15.20694	19.17367
100	4.00501	3.97054	15.62508	19.59502
110	4.00531	3.97368	16.00367	19.97736
120	4.00565	3.97633	16.34954	20.32588
130	4.00602	3.97860	16.66791	20.64652
140	4.00645	3.98058	16.96283	20.94341
150	4.00696	3.98232	17.23752	21.21985
160	4.00760	3.98388	17.49459	21.47847
170	4.00843	3.98530	17.73615	21.72145
180	4.00951	3.98661	17.96398	21.95060
190	4.01091	3.98785	18.17956	22.16742
200	4.01273	3.98905	18.38414	22.37319
210	4.01502	3.99023	18.57880	22.56903
220	4.01786	3.99142	18.76445	22.75587
230	4.02132	3.99264	18.94190	22.93455
240	4.02544	3.99392	19.11185	23.10578
250	4.03026	3.99527	19.27492	23.27020
260	4.03580	3.99672	19.43165	23.42837
270	4.04208	3.99828	19.58251	23.58080
280	4.04909	3.99997	19.72795	23.72793
290	4.05683	4.00180	19.86835	23.87015
300	4.06529	4.00377	20.00405	24.00782
310	4.07443	4.00590	20.13536	24.14127
320	4.08423	4.00819	20.26258	24.27078
330	4.09465	4.01065	20.38596	24.39662
340	4.10566	4.01328	20.50573	24.51902
350	4.11723	4.01609	20.62240	24.63820
360	4.12932	4.01906	20.73528	24.75435
370	4.14188	4.02221	20.84544	24.86766
380	4.15489	0.02553	20.95275	24.97829
390	4.16831	4.02902	21.05736	25.08639
400	4.18211	4.03267	21.15941	25.19209
450	4.25578	4.05331	21.63555	25.68886
500	4.33522	4.07749	22.06383	26.14132
550	4.41850	4.10468	22.45371	26.55839
600	4.50444	4.13440	22.81212	26.94652
650	4.59218	4.16623	23.14429	27.31052
700	4.68108	4.19982	23.45426	27.65409
750	4.77049	4.23488	23.74521	27.98010
800	4.85983	4.27115	24.01968	28.29083
850	4.94855	4.30840	24.27973	28.58813

TABLE 4c (cnd)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
900	5.03613	4.34640	24.52706	28.87346
950	5.12212	4.38497	24.76309	29.14807
1000	5.20613	4.42394	24.98900	29.41294
1050	5.28787	4.46314	25.20579	29.66894
1100	5.36709	4.50244	25.41432	29.91677
1150	5.44362	4.54171	25.61533	30.15704
1200	5.51735	4.58083	25.80945	30.39029
1300	5.65619	4.65829	26.17918	30.83747
1400	5.78355	4.73418	26.52719	31.26137
1500	5.89986	4.80808	26.85634	31.60443
1600	6.00576	4.87967	27.16895	32.04863
1700	6.10208	4.94879	27.46687	32.41566
1800	6.18967	5.01534	27.75163	32.76697
1900	6.26937	5.07927	28.02452	33.10379
2000	6.34197	5.14062	28.28662	33.42725
2100	6.40823	5.19943	28.53887	33.73830
2200	6.46881	5.25577	28.78205	34.03783
2300	6.52433	5.30974	29.01688	34.32662
2400	6.57532	5.36142	29.24396	34.60539
2500	6.62228	5.41093	29.46384	34.87477
2600	6.66562	5.45836	29.67699	35.13536
2700	6.70573	5.50383	29.88385	35.38708
2800	6.74294	5.54743	30.08480	35.63223
2900	6.77754	5.58926	30.28020	35.86946
3000	6.80980	5.62941	30.47037	36.09978
3200	6.86817	5.70505	30.83613	36.54118
3400	6.91958	5.77501	31.18412	36.95914
3600	6.96525	5.83989	31.51607	37.35597
3800	7.00644	5.90021	31.83346	37.73367
4000	7.04300	5.95645	32.13754	38.09400
4200	7.07646	6.00900	32.42945	38.43845
4400	7.10701	6.05822	32.71013	38.76836
4600	7.13505	6.10444	32.98046	39.08491
4800	7.16091	6.14793	33.24119	39.38913
5000	7.18486	6.18893	33.49300	39.68194

TABLE 4d

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$-\frac{(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
50	4.00371	3.95278	12.71364	16.66642
60	4.00369	3.96126	13.43511	17.39638
70	4.00383	3.96733	14.04622	18.01356
80	4.00406	3.97491	14.57630	18.54821
90	4.00436	3.97550	15.04434	19.01984
100	4.00469	3.97840	15.46336	19.44176
110	4.00508	3.98081	15.84265	19.82347
120	4.00554	3.98285	16.18912	20.17197
130	4.00613	3.98462	16.50799	20.49261
140	4.00695	3.98618	16.80334	20.78953
150	4.00808	3.98760	17.07841	21.06601
160	4.00968	3.98893	17.33581	21.32474
170	4.01184	3.99021	17.57767	21.56788
180	4.01472	3.99149	17.80578	21.79727
190	4.01843	3.99280	18.02163	22.01443
200	4.02305	3.99420	18.22646	22.22067
210	4.02864	3.99570	18.42138	22.41708
220	4.03526	3.99734	18.60730	22.60464
230	4.04291	3.99915	18.78502	22.78418
240	4.05158	4.00115	18.95527	22.95643
250	4.06125	4.00336	19.11865	23.12201
260	4.07187	4.00579	19.27571	23.28150
270	4.08339	4.00845	19.42694	23.43539
280	4.09574	4.01134	19.57277	23.58412
290	4.10886	4.01448	19.71359	23.72807
300	4.12267	4.01785	19.84974	23.86760
310	4.13710	4.02146	19.98154	24.00301
320	4.15210	4.02531	20.10928	24.13459
330	4.16759	4.02939	20.23321	24.26260
340	4.18353	4.03368	20.35356	24.38725
350	4.19986	4.03820	20.47055	24.50875
360	4.21653	4.04292	20.58438	24.62730
370	4.23351	4.04784	20.69521	24.74306
380	4.25076	4.05295	20.80323	24.85619
390	4.26827	4.05825	20.90858	24.96683
400	4.28598	4.06372	21.01139	25.07512
450	4.37728	4.09345	21.49171	25.58516
500	4.47224	4.12655	21.92468	26.05124
550	4.57026	4.16241	22.31965	26.48207
600	4.67083	4.20058	22.68345	26.88403

TABLE 4c (end)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$-\frac{(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
900	5.03613	4.34640	24.52706	28.87346
950	5.12212	4.38497	24.76309	29.14807
1000	5.20613	4.42394	24.98900	29.41294
1050	5.28787	4.46314	25.20570	29.66894
1100	5.36709	4.50244	25.41432	29.91677
1150	5.44362	4.54171	25.61533	30.15704
1200	5.51735	4.58083	25.80945	30.39029
1300	5.65619	4.65829	26.17918	30.83747
1400	5.78355	4.73418	26.52719	31.26137
1500	5.89986	4.80808	26.85684	31.66443
1600	6.00576	4.87967	27.16895	32.04863
1700	6.10208	4.94879	27.46687	32.41560
1800	6.18967	5.01534	27.75163	32.76697
1900	6.26937	5.07927	28.02452	33.10379
2000	6.34197	5.14062	28.28662	33.42725
2100	6.40823	5.19943	28.53887	33.73830
2200	6.46881	5.25577	28.78205	34.03783
2300	6.52438	5.30974	29.01688	34.32662
2400	6.57532	5.36142	29.24396	34.60539
2500	6.62228	5.41093	29.46384	34.87477
2600	6.66562	5.45836	29.67699	35.13536
2700	6.70573	5.50383	29.88385	35.38768
2800	6.74294	5.54743	30.08480	35.63223
2900	6.77754	5.58926	30.28020	35.86946
3000	6.80980	5.62941	30.47037	36.09978
3200	6.86817	5.70505	30.83613	36.54418
3400	6.91958	5.77501	31.18412	36.95914
3600	6.96525	5.83989	31.51607	37.35597
3800	7.00614	5.90021	31.83346	37.73367
4000	7.04300	5.95645	32.13754	38.09400
4200	7.07646	6.00900	32.42945	38.43845
4400	7.10701	6.05822	32.71013	38.76836
4600	7.13505	6.10444	32.98046	39.08491
4800	7.16091	6.14793	33.24119	39.38913
5000	7.18486	6.18893	33.49300	39.68194

TABLE 4d

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
50	4.00371	3.95278	12.71364	16.66642
60	4.00369	3.96126	13.43511	17.39638
70	4.00383	3.96733	14.04622	18.01356
80	4.00406	3.97191	14.57630	18.54821
90	4.00436	3.97550	15.04434	19.01984
100	4.00469	3.97840	15.46336	19.44176
110	4.00508	3.98081	15.84265	19.82347
120	4.00554	3.98285	16.18912	20.17197
130	4.00613	3.98462	16.50799	20.49261
140	4.00695	3.98618	16.80334	20.78953
150	4.00808	3.98760	17.07841	21.06601
160	4.00968	3.98893	17.33581	21.32474
170	4.01184	3.99021	17.57767	21.56788
180	4.01472	3.99149	17.80578	21.79727
190	4.01843	3.99280	18.02163	22.01443
200	4.02305	3.99420	18.22646	22.22067
210	4.02864	3.99570	18.42138	22.41708
220	4.03526	3.99734	18.60730	22.60464
230	4.04291	3.99915	18.78502	22.78418
240	4.05158	4.00115	18.95527	22.95643
250	4.06125	4.00336	19.11865	23.12201
260	4.07187	4.00579	19.27571	23.28150
270	4.08339	4.00845	19.42694	23.43539
280	4.09574	4.01134	19.57277	23.58412
290	4.10886	4.01448	19.71359	23.72807
300	4.12267	4.01785	19.84974	23.86760
310	4.13710	4.02146	19.98154	24.00301
320	4.15210	4.02531	20.10928	24.13459
330	4.16759	4.02939	20.23321	24.26260
340	4.18353	4.03368	20.35356	24.38725
350	4.19986	4.03820	20.47055	24.50875
360	4.21653	4.04292	20.58438	24.62730
370	4.23351	4.04784	20.69521	24.74306
380	4.25076	4.05295	20.80323	24.85619
390	4.26827	4.05825	20.90858	24.96683
400	4.28598	4.06372	21.01139	25.07512
450	4.37738	4.09345	21.49171	25.58516
500	4.47224	4.12655	21.92468	26.05124
550	4.57026	4.16241	22.31965	26.48207
600	4.67083	4.20058	22.68345	26.88403

TABLE 4d (end)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
650	4.77323	4.24068	23.02124	27.26193
700	4.87652	4.28241	23.33703	27.61944
750	4.97967	4.32545	23.63395	27.95941
800	5.08169	4.36954	23.91451	28.28405
850	5.18170	4.41438	24.18075	28.59514
900	5.27897	4.45973	24.43436	28.89409
950	5.37295	4.50534	24.67670	29.18204
1000	5.46324	4.55099	24.90896	29.45995
1050	5.54958	4.59650	25.13210	29.72861
1100	5.63185	4.64171	25.34698	29.98869
1150	5.71001	4.68647	25.55430	30.24078
1200	5.78409	4.73068	25.75469	30.48537
1300	5.92044	4.81705	26.13678	30.95383
1400	6.04203	4.90029	26.49683	31.39712
1500	6.15030	4.98009	26.83765	31.81774
1600	6.24672	5.05630	27.16151	32.21781
1700	6.33273	5.12890	27.47025	32.59915
1800	6.40963	5.19795	27.76538	32.96334
1900	6.47860	5.26357	28.04819	33.31177
2000	6.54065	5.32590	28.31977	33.64568
2100	6.59660	5.38511	28.58107	33.96618
2200	6.64747	5.44135	28.83290	34.27425
2300	6.69366	5.49481	29.07596	34.57078
2400	6.73583	5.54565	29.31090	34.85656
2500	6.77447	5.59404	29.53828	35.13233
2600	6.80990	5.64014	29.75858	35.39873
2700	6.84277	5.68408	29.97228	35.65636
2800	6.87312	5.72601	30.17976	35.90577
2900	6.90129	5.76606	30.38139	36.14746
3000	6.92754	5.80434	30.57752	36.38187
3200	6.97503	5.87606	30.95445	36.83051
3400	7.01693	5.94196	31.31269	37.25465
3600	7.05426	6.00274	31.65406	37.65681
3800	7.08781	6.05898	31.98014	38.03912
4000	7.11821	6.11119	32.29227	38.40347
4200	7.14596	6.15982	32.59163	38.75145
4400	7.17143	6.20523	32.87924	39.08448
4600	7.19496	6.24775	33.15602	39.40378
4800	7.21679	6.28768	33.42278	39.71047
5000	7.23713	6.32526	33.68022	40.00549

TABLE 4c

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
50	4.00386	3.95100	13.24697	17.19798
60	4.00380	3.95980	13.96815	17.92796
70	4.00391	3.96610	14.57906	18.54516
80	4.00413	3.97084	15.10898	19.07982
90	4.00441	3.97455	15.57690	19.55145
100	4.00473	3.97755	15.99582	19.97338
110	4.00508	3.98004	16.37504	20.35509
120	4.00545	3.98214	16.72144	20.70359
130	4.00588	3.98395	17.04026	21.02421
140	4.00637	3.98553	17.33556	21.32110
150	4.00698	3.98694	17.61058	21.59753
160	4.00777	3.98822	17.86794	21.85616
170	4.00882	3.98940	18.10976	22.09916
180	4.01020	3.99051	18.33782	22.32833
190	4.01201	3.99159	18.55360	22.54520
200	4.01433	3.99267	18.75837	22.75105
210	4.01726	3.99377	18.95320	22.94698
220	4.02087	3.99492	19.13902	23.13394
230	4.02521	3.99614	19.31663	23.31277
240	4.03034	3.99745	19.48673	23.48418
250	4.03620	3.99888	19.64994	23.64883
260	4.04308	4.00045	19.80681	23.80727
270	4.05072	4.00217	19.95782	23.95999
280	4.05921	4.00405	20.10340	24.10746
290	4.06854	4.00611	20.24395	24.25006
300	4.07867	4.00836	20.37980	24.38816
310	4.08960	4.01080	20.51127	24.52208
320	4.10128	4.01345	20.63865	24.65210
330	4.11369	4.01629	20.76219	24.77849
340	4.12679	4.01935	20.88214	24.90149
350	4.14053	4.02261	20.99869	25.02131
360	4.15488	4.02609	21.11206	25.13815
370	4.16979	4.02977	21.22242	25.25220
380	4.18523	4.03366	21.32994	25.36360
390	4.20116	4.03774	21.43477	25.47252
400	4.21754	4.04203	21.53705	25.57909
450	4.30507	4.06632	22.01449	26.08082
500	4.39927	4.09486	22.44436	26.53923
550	4.49734	4.12697	22.83613	26.96310
600	4.59710	4.16199	23.19670	27.35869

TABLE 4c (end)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
650	4.69720	4.19931	23.53130	27.73061
700	4.79656	4.23843	23.84393	28.08236
750	4.89441	4.27891	24.13772	28.41663
800	4.99019	4.32038	24.41519	28.73558
850	5.08348	4.36254	24.67838	29.04092
900	5.17398	4.40512	24.92894	29.33406
950	5.26146	4.44790	25.16826	29.61616
1000	5.34577	4.49070	25.39740	29.88820
1050	5.42682	4.53336	25.61763	30.15099
1100	5.50456	4.57575	25.82950	30.40526
1150	5.57899	4.61776	26.03383	30.65160
1200	5.65014	4.65931	26.23124	30.89055
1300	5.78286	4.74071	26.60741	31.34813
1400	5.90340	4.81953	26.96164	31.78117
1500	6.01267	4.89549	27.29676	32.19225
1600	6.11162	4.96845	27.61505	32.58351
1700	6.20126	5.03838	27.91838	32.95676
1800	6.28252	5.10528	28.20827	33.31355
1900	6.35632	5.16921	28.48603	33.65524
2000	6.42345	5.23027	28.75274	33.98301
2100	6.48466	5.28857	29.00934	34.29792
2200	6.54060	5.34423	29.25666	34.60089
2300	6.59186	5.39737	29.49541	34.89278
2400	6.63896	5.44814	29.72620	35.17434
2500	6.68234	5.49665	29.94959	35.44635
2600	6.72244	5.54303	30.16608	35.70912
2700	6.75953	5.58741	30.37612	35.96353
2800	6.79400	5.62989	30.58009	36.20999
2900	6.82608	5.67060	30.77837	36.44897
3000	6.85603	5.70962	30.97127	36.68090
3200	6.91034	5.78300	31.34214	37.12514
3400	6.95832	5.85075	31.69479	37.54555
3600	7.00108	5.91350	32.03101	37.94451
3800	7.03950	5.97177	32.35232	38.32409
4000	7.07426	6.02604	32.66003	38.68606
4200	7.10593	6.07672	32.95528	39.03200
4400	7.13496	6.12417	33.23907	39.36324
4600	7.16170	6.16870	33.51230	39.68100
4800	7.18645	6.21060	33.77573	39.98633
5000	7.20947	6.25010	34.03006	40.28017

TABLE 4f

T, °K	$\frac{C_p^0}{R}$	$\frac{\left(H^0 - E_0^0\right)}{RT}$	$-\frac{\left(\Phi^0 - E_0^0\right)}{RT}$	$\frac{S^0}{R}$
50	4.00315	3.96348	13.74166	17.70514
60	4.00328	3.97010	14.46491	18.43501
70	4.00352	3.97486	15.07728	19.05214
80	4.00382	3.97846	15.60829	19.58675
90	4.00417	3.98130	16.07706	20.05836
100	4.00455	3.98360	16.49665	20.48026
110	4.00501	3.98553	16.87642	20.86195
120	4.00561	3.98717	17.22328	21.21046
130	4.00644	3.98862	17.54248	21.53111
140	4.00764	3.98994	17.83812	21.82806
150	4.00938	3.99117	18.11344	22.10462
160	4.01180	3.99238	18.37106	22.36345
170	4.01507	3.99361	18.61314	22.60676
180	4.01932	3.99492	18.84144	22.83637
190	4.02465	3.99634	19.05748	23.05382
200	4.03115	3.99791	19.26250	23.26042
210	4.03884	3.99967	19.45760	23.45728
220	4.04773	4.00165	19.64371	23.64337
230	4.05780	4.00387	19.82164	23.82551
240	4.06900	4.00635	19.99209	23.99844
250	4.08127	4.00909	20.15570	24.16479
260	4.09453	4.01212	20.31299	24.32512
270	4.10871	4.01543	20.46447	24.47991
280	4.12371	4.01903	20.61057	24.62961
290	4.13947	4.02291	20.75167	24.77459
300	4.15590	4.02707	20.88812	24.91520
310	4.17293	4.03150	21.02024	25.05174
320	4.19049	4.03619	21.14831	25.18450
330	4.20853	4.04114	21.27259	25.31373
340	4.22698	4.04633	21.39330	25.43964
350	4.24580	4.05176	21.51067	25.56244
360	4.26496	4.05742	21.62489	25.68231
370	4.28441	4.06329	21.73614	25.79943
380	4.30413	4.06937	21.84458	25.91395
390	4.32410	4.07564	21.95037	26.02601
400	4.34429	4.08210	22.05364	26.13574
450	4.44813	4.11696	22.53641	26.65338
500	4.55581	4.15544	22.97214	27.12758
550	4.66632	4.19684	23.37012	27.56696
600	4.77855	4.24063	23.73715	27.97779

TABLE 4f (end)

T, °K	$\frac{C_p^0}{R}$	$\frac{\left(H^0 - E_0^0\right)}{RT}$	$-\frac{\left(\Phi^0 - E_0^0\right)}{RT}$	$\frac{S^0}{R}$
650	4.89126	4.28635	24.07838	28.36473
700	5.00318	4.33356	24.39775	28.73131
750	5.11314	4.38188	24.69838	29.08026
800	5.22017	4.43095	24.98274	29.41369
850	5.32348	4.48043	25.25285	29.73328
900	5.42253	4.53004	25.51035	30.04039
950	5.51697	4.57952	25.75660	30.33612
1000	5.60662	4.62865	25.99275	30.62141
1050	5.69142	4.67726	26.21976	30.89703
1100	5.77143	4.72519	26.43846	31.16366
1150	5.84676	4.77234	26.64955	31.42189
1200	5.91758	4.81859	26.85363	31.67223
1300	6.04659	4.90820	27.24289	32.15110
1400	6.16028	4.99366	27.60978	32.60345
1500	6.26052	5.07484	27.95710	33.03195
1600	6.34910	5.15177	28.28711	33.43888
1700	6.42761	5.22456	28.60164	33.82620
1800	6.49744	5.29337	28.90223	34.19561
1900	6.55979	5.35841	29.19019	34.54861
2000	6.61571	5.41991	29.46662	34.88653
2100	6.66606	5.47807	29.73247	35.21055
2200	6.71160	5.53312	29.98860	35.52172
2300	6.75296	5.58527	30.23571	35.82099
2400	6.79068	5.63472	30.47448	36.10920
2500	6.82521	5.68166	30.70546	36.38712
2600	6.85695	5.72626	30.92917	36.65544
2700	6.88623	5.76869	31.14609	36.91478
2800	6.91334	5.80909	31.35662	37.16571
2900	6.93852	5.84761	31.56114	37.40870
3000	6.96199	5.88437	31.76001	37.64438
3200	7.00451	5.95308	32.14200	38.09509
3400	7.04208	6.01605	32.50482	38.52088
3600	7.07563	6.07400	32.85036	38.92436
3800	7.10587	6.12753	33.18021	39.30775
4000	7.13334	6.17714	33.49579	39.67294
4200	7.15847	6.22328	33.79831	40.02159
4400	7.18162	6.26633	34.08882	40.35515
4600	7.20305	6.30659	34.36826	40.67486
4800	7.22299	6.34436	34.63748	40.98185
5000	7.24162	6.37989	34.89719	41.27709

TABLE 4g

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$-\frac{(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
50	4.00292	3.96809	13.38370	17.35180
60	4.00341	3.97391	14.10771	18.08163
70	4.00339	3.97810	14.72063	18.69874
80	4.00373	3.98129	15.25205	19.23334
90	4.00411	3.98380	15.72112	19.70493
100	4.00457	3.98585	16.14097	20.12683
110	4.00520	3.98758	16.52095	20.50853
120	4.00612	3.98908	16.86798	20.85707
130	4.00753	3.99045	17.18733	21.17778
140	4.00964	3.99174	17.48310	21.47484
150	4.01264	3.99302	17.75855	21.75158
160	4.01676	3.99437	18.01629	22.01067
170	4.02214	3.99584	18.25849	22.25434
180	4.02890	3.99748	18.48694	22.48442
190	4.03709	3.99935	18.70312	22.70247
200	4.04673	4.00147	18.90831	22.90978
210	4.05777	4.00388	19.10360	23.10749
220	4.07017	4.00661	19.28992	23.29654
230	4.08382	4.00966	19.46809	23.47776
240	4.09862	4.01306	19.63881	23.65187
250	4.11447	4.01679	19.80271	23.81951
260	4.13124	4.02087	19.96033	23.98120
270	4.14883	4.02528	20.11216	24.13744
280	4.16714	4.03002	20.25863	24.28866
290	4.18606	4.03507	20.40014	24.43522
300	4.20552	4.04043	20.53702	24.57746
310	4.22545	4.04607	20.66960	24.71568
320	4.24579	4.05200	20.79815	24.85015
330	4.26649	4.05818	20.92293	24.98112
340	4.28750	4.06462	21.04417	25.10880
350	4.30880	4.07129	21.16209	25.23339
360	4.33036	4.07819	21.27688	25.35507
370	4.35215	4.08530	21.38872	25.47402
380	4.37416	4.09261	21.49776	25.59037
390	4.39637	4.10014	21.60417	25.70428
400	4.41879	4.10780	21.70807	25.81587
450	4.53356	4.14869	22.19422	26.34291
500	4.65215	4.19308	22.63360	26.82668
550	4.77338	4.24031	23.03544	27.27575
600	4.89567	4.28982	23.40650	27.69633

TABLE 4g (end)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$-\frac{(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
650	5.01732	4.34112	23.75188	28.09300
700	5.13671	4.39370	24.07551	28.46922
750	5.25253	4.44712	24.38047	28.82759
800	5.36377	4.50096	24.66919	29.17015
850	5.46976	4.55485	24.94368	29.49854
900	5.57010	4.60850	25.20555	29.81405
950	5.66463	4.66162	25.45614	30.11777
1000	5.75336	4.71401	25.69659	30.41061
1050	5.83641	4.76550	25.92784	30.69335
1100	5.91401	4.81597	26.15070	30.96667
1150	5.98642	4.86530	26.36587	31.23117
1200	6.05396	4.91344	26.57396	31.48740
1300	6.17563	5.00596	26.97093	31.97689
1400	6.28151	5.09337	27.34514	32.43852
1500	6.37390	5.17573	27.69938	32.87512
1600	6.45484	5.25320	28.03592	33.28912
1700	6.52606	5.32602	28.35660	33.68263
1800	6.58904	5.39448	28.66298	34.05747
1900	6.64501	5.45885	28.95639	34.41525
2000	6.69502	5.51943	29.23795	34.75739
2100	6.73992	5.57650	29.50864	35.08514
2200	6.78044	5.63032	29.76931	35.39964
2300	6.81718	5.68114	30.02072	35.70186
2400	6.85065	5.72918	30.26353	35.99272
2500	6.88127	5.77066	30.49834	36.27300
2600	6.90940	5.81777	30.72567	36.54345
2700	6.93535	5.85869	30.94601	36.80470
2800	6.95939	5.89757	31.15979	37.05737
2900	6.98173	5.93458	31.36739	37.30198
3000	7.00256	5.96983	31.56918	37.53902
3200	7.04034	6.03558	31.95660	37.99219
3400	7.07379	6.09569	32.32433	38.42003
3600	7.10373	6.15088	32.67434	38.82522
3800	7.13077	6.20175	33.00828	39.21004
4000	7.15537	6.24883	33.32760	39.57643
4200	7.17793	6.29254	33.63355	39.92610
4400	7.19873	6.33326	33.92723	40.26050
4600	7.21801	6.37132	34.20961	40.58093
4800	7.23596	6.40697	34.48153	40.88851
5000	7.25273	6.44047	34.74376	41.18424

Influence of Hydrogen Isotopes on the Thermodynamic Functions of Free Radicals – Oxygen and Sulfur Hydrides, after Haar and Friedman [5].

TABLE 5a

Principal Molecular Constants Used for Calculation of the Thermal Properties of Radicals (in the form of an ideal gas).

Constant	measurement unit	OH	OD	OT	SH	SD	ST
ν	cm^{-1}	3569.6	2632.5	2221	2582	1878	1567
$x_e\,\omega_e/\nu$	Dimensionless	0.0232	0.0168	0.014	0.0232	0.017	0.014
δ	"	0.0384	0.0304	0.023	0.0317	0.0225	0.019
B_0	cm^{-1}	18.514	9.868	6.97	9.461	4.900	3.40
ρ	$°K^{-1}$	7.59×10^{-6}	7.59×10^{-6}	7.59×10^{-6}	7.5×10^{-6}	7.5×10^{-6}	7.5×10^{-6}
A	cm^{-1}	—139.7	—139.7	—139.7	—376.96	—376.96	—376.96

TABLE 5b

Thermodynamic Functions of OH (as ideal gas).

$T, °K$	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$\frac{-(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
50	3.50050	2.87580	12.59278	15.46858
70	3.73237	3.09296	13.59680	16.68976
90	3.80047	3.24458	14.39361	17.63819
110	3.79879	3.34611	15.05523	18.40134
130	3.77249	3.41389	15.62010	19.03399
150	3.74051	3.45958	16.11202	19.57160
170	3.70993	3.49080	16.54706	20.03786
190	3.68295	3.51241	16.93658	20.44899
210	3.65993	3.52753	17.28891	20.81644
230	3.64053	3.53817	17.61033	21.14850
250	3.62424	3.54568	17.90567	21.45135
300	3.59395	3.55608	18.55318	22.10926
350	3.57393	3.55997	19.10164	22.66161
400	3.56053	3.56081	19.57714	23.13795
450	3.55189	3.56027	19.99653	23.55680
500	3.54721	3.55916	20.37158	23.93074
600	3.54912	3.55712	21.02029	24.57741
700	3.56602	3.55700	21.56859	25.12559
800	3.59683	3.55992	22.04372	25.60364
900	3.63880	3.56627	22.46334	26.02961
1000	3.68844	3.57596	22.83956	26.41552
1100	3.74245	3.58861	23.18096	26.76957
1200	3.79811	3.60375	23.49384	27.09759
1300	3.85345	3.62083	23.78296	27.40379
1400	3.90711	3.63938	24.05197	27.69135
1500	3.95832	3.65895	24.30372	27.96267
1600	4.00660	3.67918	24.54050	28.21968
1700	4.05179	3.69979	24.76417	28.46396
1800	4.09386	4.72052	24.97623	28.69675
1900	4.13294	3.74121	25.17794	28.91915
2000	4.16916	3.76172	25.37037	29.13209
2200	4.23382	3.80177	25.73079	29.53256
2400	4.28949	3.84015	26.06324	29.90339
2600	4.33769	3.87661	26.37207	30.24868
2800	4.37974	3.91108	26.66063	30.57171
3000	4.41674	3.94359	26.93159	30.87518
4200	4.44962	3.97420	27.18709	31.16129
3400	4.47905	4.00305	27.42890	31.43195
3600	4.50564	4.03025	27.65849	31.68874
3800	4.52985	4.05592	27.87708	31.93300
4000	4.55208	4.08017	28.08574	32.16591
4200	4.57262	4.10314	28.28538	32.38852
4400	4.59173	4.12492	28.47676	32.60168
4600	4.60962	4.14561	28.66058	32.80619
4800	4.62645	4.16529	28.83744	33.00273
5000	4.64238	4.18406	29.00786	33.19192

TABLE 5c

Thermodynamic Functions of OD (as ideal gas)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$-\frac{(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
1	2	3	4	5
50	3.68420	3.13107	12.94356	16.07463
70	3.84240	3.31558	14.02836	17.34394
90	3.87567	3.43794	14.87746	18.31540
110	3.85244	3.51589	15.57553	19.09142
130	3.81171	3.56462	16.16713	19.73175
150	3.76978	3.59474	16.67951	20.27425
170	3.73221	3.61306	17.13067	20.74378
190	3.70024	3.62388	17.53319	21.15707
210	3.67360	3.62985	17.89619	21.52604
230	3.65153	3.63266	18.22656	21.85022
250	3.63325	3.62341	18.52949	22.16290
300	3.60014	3.63041	19.19175	22.82216
350	3.58007	3.62453	19.75095	23.37548
400	3.56994	3.61824	20.24454	23.85278
450	3.56856	3.61272	20.66038	24.27310
500	3.57536	3.60858	21.04079	24.64937
600	3.61036	3.60560	21.69832	25.30392
700	3.66664	3.61011	22.25438	25.86449
800	3.73487	3.62135	22.73711	26.35846
900	3.80736	3.63798	23.16456	26.80254
1000	3.87889	3.65852	23.54889	27.20741
1100	3.94086	3.68169	23.89866	27.58035
1200	4.00937	3.[illegible]0644	24.22006	27.92650
1300	4.06663	3.73199	24.51774	28.24973
1400	4.11816	3.75776	24.79525	28.55301
1500	4.16451	3.78336	25.05539	28.83875
1600	4.20615	3.80851	25.30036	29.10887
1700	4.24360	3.83302	25.53199	29.36501
1800	4.27734	3.85678	25.75176	29.60854
1900	4.30784	3.87973	25.96090	29.84063
2000	4.33549	3.90184	26.16048	30.06232
2200	4.38365	3.94351	26.53484	30.47785
2400	4.42419	3.98193	26.87914	30.86107
2600	4.45883	4.01731	27.19929	31.21660
2800	4.48892	4.04995	27.49821	31.54816
3000	4.51542	4.08011	27.77867	31.85878
3200	4.53907	4.10807	28.04290	32.15097
3400	4.56043	4.13407	28.29274	32.42681
3600	4.57994	4.15830	28.52972	32.68802
3800	4.59793	4.18098	28.75518	32.93616
4000	4.61466	4.20225	28.97017	33.17242
4200	4.63035	4.22226	29.17570	33.39796
4400	4.64516	4.24115	29.37254	33.61369
4600	4.65920	4.25902	29.56147	33.82049
4800	4.67261	4.27597	29.74310	34.01907
5000	4.68548	4.29211	29.91799	34.21010

TABLE 5d

Thermodynamic Functions of OT (as ideal gas)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^\circ-E_0^0)}{RT}$	$-\frac{(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
1	2	3	4	5
50	3.72686	3.24159	13.23305	16.47464
70	3.87087	3.40436	14.35131	17.75567
90	3.89672	3.51244	15.22089	18.73333
110	3.86809	3.58015	15.93286	19.51301
130	3.82340	3.62108	16.53455	20.15563
150	3.77861	3.64503	17.05456	20.69959
170	3.73897	3.65835	17.51170	21.17005
190	3.70553	3.66503	17.91902	21.58405
210	3.67781	3.66753	18.28597	21.95350
230	3.65504	3.66739	18.61953	22.28702
250	3.63639	3.66564	18.92535	22.59099
300	3.60407	3.65781	19.59303	23.25084
350	3.58807	3.64882	20.15621	23.80503
400	3.58579	3.64095	20.64290	24.28385
450	3.59563	3.63526	21.07140	24.70666
500	3.61579	3.63223	21.45423	25.08646
600	3.67869	3.63439	22.11650	25.75089
700	3.75808	3.64628	22.67751	26.32379
800	3.84162	3.66549	23.16560	26.83109
900	3.92209	3.68957	23.59869	27.28826
1000	3.99601	3.71658	23.98880	27.70538
1100	4.06224	3.74506	24.34435	28.08941
1200	4.12082	3.77398	24.67146	28.44544
1300	4.17236	3.80268	24.97467	28.77735
1400	4.21767	3.83074	25.25752	29.08826
1500	4.25752	3.85790	25.52274	29.38064
1600	4.29277	3.88399	25.77256	29.65655
1700	4.32403	3.90897	26.00879	29.91776
1800	4.35191	3.93283	26.23289	30.16572
1900	4.37689	3.95555	26.44614	30.40169
2000	4.39942	3.97719	26.64960	30.62679
2200	4.43846	4.01740	27.03059	31.04799
2400	4.47121	4.05389	27.38173	31.43562
2600	4.49925	4.08709	27.70756	31.79465
2800	4.52369	4.11742	28.01157	32.12899
3000	4.54533	4.14525	28.29660	32.44185
3200	4.56480	4.17087	28.56496	32.73583
3400	4.58253	4.19457	28.81854	33.01311
3600	4.59884	4.21659	29.05892	33.27551
3800	4.61403	4.23710	29.28746	33.52456
4000	4.62828	4.25632	29.50528	33.76160
4200	4.64174	4.27435	29.71340	33.98775
4400	4.65456	4.29134	29.91263	34.20397
4600	4.66681	4.30740	30.10374	34.41114
4800	4.67859	4.32263	30.28739	34.61002
5000	4.68996	4.33709	30.46415	34.80124

TABLE 5e

Thermodynamic Functions of SH (as ideal gas)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$-\frac{(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
1	2	3	4	5
50	3.42506	3.07447	13.84212	16.91659
70	3.49225	3.18495	14.89561	18.08056
90	3.56468	3.26090	15.70560	18.96650
110	3.65267	3.32402	16.36621	19.69023
130	3.73955	3.38137	16.92620	20.30757
150	3.81216	3.43417	17.41385	20.84802
170	3.86524	3.48197	17.84667	21.32864
190	3.89915	3.52425	18.23631	21.76056
210	3.91700	3.56094	18.59015	22.15109
230	3.92266	3.59224	18.91493	22.50717
250	3.91876	3.61857	19.21558	22.83415
300	3.88685	3.66624	19.87989	23.54613
350	3.84457	3.69475	20.44738	24.14213
400	3.80599	3.71099	20.94191	24.65290
450	3.77600	3.71983	21.37957	25.09940
500	3.75911	3.72455	21.77177	25.49632
600	3.75551	3.72947	22.45129	26.18076
700	3.78465	3.73496	23.02658	26.76154
800	3.83346	3.74408	23.52586	27.26994
900	3.89168	3.75720	23.96758	27.72478
1000	3.95250	3.77369	24.36426	28.13795
1100	4.01498	3.79266	24.72481	28.51747
1200	4.06806	3.81329	25.05568	28.86897
1300	4.11986	3.83492	25.36176	29.19668
1400	4.16714	3.85699	25.64677	29.50376
1500	4.21007	3.87912	25.91362	29.79274
1600	4.24893	3.90104	26.16468	30.06572
1700	4.28412	3.92255	26.40183	30.32438
1800	4.31603	3.94354	26.62663	30.57017
1900	4.34504	3.96393	26.84039	30.80432
2000	4.37451	3.98365	27.04423	31.02788
2200	4.41798	4.02109	27.42568	31.44677
2400	4.45751	4.05585	27.77707	31.83292
2600	4.49166	4.08809	28.10301	32.19110
2800	4.52163	4.11800	28.40708	32.52508
3000	4.54828	4.14582	28.69216	32.83798
3200	4.57229	4.17173	28.96056	33.13229
3400	4.59418	4.19595	29.21420	33.41015
3600	4.61433	4.21864	29.45469	33.67333
3800	4.63306	4.23996	29.68336	33.92332
4000	4.65061	4.26006	29.90135	34.16141
4200	4.66716	4.27905	30.10967	34.38872
4400	4.68288	4.29706	30.30914	34.60620
4600	4.69789	4.31416	30.50054	34.81470
4800	4.71228	4.33045	30.68449	35.01494
5000	4.72613	4.34601	30.86159	35.20760

TABLE 5f

Thermodynamic Functions of SD (as ideal gas)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$-\frac{(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
1	2	3	4	5
50	3.48664	3.26071	14.32377	17.58448
70	3.51771	3.32913	15.43278	18.76191
90	3.58009	3.37736	16.27543	19.65279
110	3.66486	3.42176	16.95749	20.37925
130	3.75097	3.46588	17.53266	20.99854
150	3.82360	3.50894	18.03169	21.54063
170	3.87679	3.54928	18.47339	22.02267
190	3.91073	3.58568	18.87019	22.45587
210	3.92844	3.61788	19.23055	22.84843
230	3.93377	3.64566	19.56083	23.20649
250	3.93034	3.66853	19.86578	23.53431
300	3.90366	3.71015	20.53861	24.24876
350	3.87446	3.73562	21.11262	24.84824
400	3.85665	3.75172	21.61257	25.36429
450	3.85359	3.76307	22.05514	25.81821
500	3.86384	3.77253	22.45211	26.22464
600	3.91185	3.79136	23.14156	26.93292
700	3.97770	3.81317	23.72759	27.54076
800	4.04682	3.83808	24.23837	28.07645
900	4.11213	3.86495	24.69197	28.55692
1000	4.17099	3.89267	25.10061	28.99328
1100	4.22289	3.92038	25.47293	29.39331
1200	4.26824	3.94752	25.81521	29.76273
1300	4.30782	3.97374	26.13223	30.10597
1400	4.34246	3.99888	26.42764	30.42652
1500	4.37291	4.02282	26.70437	30.72719
1600	4.39985	4.04556	26.96471	31.01027
1700	4.42383	4.06711	27.21064	31.27775
1800	4.44534	4.08754	27.44368	31.53122
1900	4.46477	4.10689	27.66520	31.77209
2000	4.48242	4.12524	27.87634	32.00158
2200	4.51348	4.15915	28.27113	32.43028
2400	4.55012	4.18982	28.63437	32.82419
2600	4.56347	4.21769	28.97082	33.18851
2800	4.58433	4.24313	29.28435	33.52748
3000	4.60328	4.26653	29.57791	33.84444
3200	4.62072	4.28812	29.85398	34.14210
3400	4.63697	4.30818	30.11454	34.42272
3600	4.65225	4.32688	30.36192	34.68820
3800	4.66674	4.34438	30.59575	34.94013
4000	4.68056	4.36084	30.81901	35.17985
4200	4.69386	4.37639	31.03215	35.40854
4400	4.70667	4.39111	31.23609	35.62720
4600	4.71909	4.40510	31.43158	35.83668
4800	4.73117	4.41843	31.61935	36.03778
5000	4.74294	4.43119	31.79997	36.23116

TABLE 5g

Thermodynamic Functions of ST (as ideal gas)

T, °K	$\frac{C_p^0}{R}$	$\frac{(H^0-E_0^0)}{RT}$	$-\frac{(\Phi^0-E_0^0)}{RT}$	$\frac{S^0}{R}$
1	2	3	4	5
50	3.49544	3.32989	14.65352	17.98341
70	3.52224	3.38031	15.78265	19.16296
90	3.58359	3.41804	16.63681	20.05485
110	3.66840	3.45567	17.32637	20.78204
130	3.75473	3.49512	17.90691	21.40203
150	3.82752	3.53478	18.40994	21.94472
170	3.88086	3.57254	18.85483	22.42737
190	3.91513	3.60692	19.25426	22.86118
210	3.93388	3.63743	19.61629	23.25372
230	3.94115	3.66377	19.94742	23.61119
250	3.94094	3.68599	20.25444	23.94043
300	3.92745	3.72747	20.93021	24.65768
350	3.91718	3.75517	21.50702	25.26219
400	3.92035	3.77547	22.00983	25.78530
450	3.93602	3.79238	22.45551	26.24789
500	3.96340	3.80809	22.85590	26.66399
600	4.03161	3.83949	23.55296	27.39245
700	4.10887	3.87213	24.14727	28.01940
800	4.17065	3.90535	24.06647	28.57182
900	4.22912	3.93816	25.12836	29.06652
1000	4.27916	3.96982	25.54494	29.51476
1100	4.32179	3.99904	25.92472	29.92466
1200	4.35816	4.02831	26.27399	30.30230
1300	4.38943	4.05492	26.59750	30.65242
1400	4.41686	4.07944	20.89893	30.97837
1500	4.44020	4.10305	27.18121	31.28426
1600	4.46140	4.12452	27.44671	31.57123
1700	4.47977	4.14513	27.69738	31.84251
1800	4.49656	4.16419	27.93487	32.09906
1900	4.51179	4.18210	28.16050	32.34260
2000	4.52572	4.19893	28.37545	32.57438
2200	4.55050	4.22980	28.77712	33.00692
2400	4.57213	4.25746	29.14686	33.40382
2600	4.59144	4.28240	29.48815	33.77055
2800	4.60900	4.30511	29.80635	34.11146
3000	4.62524	4.32592	30.10410	34.43002
3200	4.64042	4.34510	30.38391	34.72901
3400	4.65477	4.36290	30.64788	35.01078
3600	4.66845	4.37950	30.89772	35.27722
3800	4.68157	4.39505	31.13493	35.52998
4000	4.69424	4.40968	31.36075	35.77043
4200	4.70653	4.42355	31.57623	35.99978
4400	4.71847	4.43668	31.78232	36.21900
4600	4.73014	4.44924	31.97982	36.42906
4800	4.74156	4.74156	32.16943	36.63055
5000	4.75275	4.47257	32.35176	36.82433

TABLE 6

Thermodynamic Functions of Isotopic Molecules of Methylacetylene and Acetylene, after Zeise [3]

Molar heat capacities, C_p, cal / mole · degree^{-1}			Enthalpies, $H^0 - E_0^0$ cal / mole		Function $-\frac{(\Phi^0-E^0)}{T}$, cal / mole					
T, °K	Methyl-acetylene	Methyldeutero-acetylene	Methyl-acetylene	Methyldeutero-acetylene	Methyl-acetylene	Methyldeutero-acetylene	T, °K	C_2H_2 (188)	C_2HD (188)	C_2D_2 (188)
1000	27.71	28.13	18670	19110	65.86	66.90				
900	26.51	—	15956	—	63.94	—	700	47.957	50.198	50.510
800	25.14	25.55	13372	13728	61.91	62.85	600	46.330	48.516	48.675
700	23.58	—	10935	—	59.76	—	500	44.517	46.637	46.639
600	21.80	22.20	8663	8940	57.44	58.24	373.2	41.844	43.868	43.587
500	19.74	—	6584	—	54.92	—	298.2	39.975	41.935	41.447
400	17.33	17.84	4728	4916	52.14	52.76	273.2	39.281	41.232	40.563
300	14.55	—	3131	—	48.95	—				
298.16	14.55	15.16	3104	3235	48.89	49.36				
250	—	13.78	—	2537	—	47.52				

TABLE 7

Isotope Effects in Vapor Pressures [6]

T, °C	p_H/p_D Isopropyl alcohols	n-Butyl alcohols	Anilines	Acetic acids	Butyric acids	Isobutyric acids	Isovaleric acid
15	1.065	—	—	0.981	—	—	—
20	1.062	1.063	—	0.977	—	—	—
25	—	—	—	0.975	—	—	—
30	1.055	1.059	—	0.973	—	—	—
35	—	—	—	0.972	—	—	—
40	1.048	1.054	—	0.970	—	—	—
45	—	—	—	0.969	—	—	—
50	1.042	1.050	1.036	0.968	0.990	0.985	—
55	—	—	1.026	0.969	0.981	0.981	0.967_0
60	1.037	1.046	1.019	0.971	0.972	0.978	0.965_7
65	—	—	1.014	0.974	0.964	0.974	0.964_7
70	1.033	1.042	1.011	0.977	0.955	0.972	0.963_9
75	—	—	1.008	0.979	0.948	0.969	0.963_4
80	1.029	1.038	1.006	0.980	0.943	0.966	0.963_0
85	—	—	—	0.981	0.945	0.964	0.962_8
90	—	1.034	—	0.982	0.948	0.961	0.962_6
95	—	1.034	—	0.982_4	0.950	—	0.962_5
100	—	1.031	—	0.982_8	0.953	—	0.962_4
105	—	—	—	—	0.956	—	0.962_3
110	—	—	—	0.983_3	0.959	—	0.962_2
115	—	—	—	—	0.962	—	—

TABLE 8

Isotope Effects in Heats of Vaporization [6]

Temperature range, °C	$\lambda_D - \lambda_H$,* cal / mole Isopropyl alcohols	n-Butyl alcohols	Anilines	Acetic acids	Butyric acids
15–30	—	—	—	90	—
20–30	—	90	—	—	—
20–40	130	—	—	—	—
30–50	—	80	—	60	—
40–60	100	—	—	—	—
50–60	—	—	340	−80	—
60–70	90	90	190	—	—
70–80	90	—	110	−70	—
50–80	—	—	—	—	350
70–90	—	90	—	—	—
80–90	—	—	—	—	−110
90–100	—	90	—	—	−150
80–100	—	—	—	−30	—
100–110	—	—	—	−10	−170

---

* p_D, λ_D and p_H, λ_H are the pressures and the heats of vaporization of the deutero-compound and its hydrogen analog, respectively.

LITERATURE CITED

[1] J. Bigeleisen and M. Mayer, J. Chem. Phys. 15, 261 (1947).

[2] J. Bigeleisen, J. Chem. Phys. 21, 1333 (1953).

[3] F. Zeise, Thermodynamik B. III/1 (1954).

[4] A. S. Friedman and L. Haar, J. Chem. Phys. 22, 2051 (1954).

[5] L. Haar and A. S. Friedman, J. Chem. Phys. 23, No. 5, 869 (1955).

[6] I. B. Rabinovich, N. N. Sokolov and P. I. Artyukhin, Proc. Acad. Sci. USSR 105, 762 (1955).

II. TABLES OF ISOTOPIC EXCHANGE EQUILIBRIUM CONSTANTS

TABLE 1

Ratios of the Vibrational Statistical Sums Q_2/Q_1 and Equilibrium Constants for the Isotopic Exchange of Nitrogen and Its Compounds, after Urey [1]

	$\frac{N^{15}H_4^+}{N^{14}H_4^+}$	$\left(\frac{N_2^{15}}{N_2^{14}}\right)^{1/2}$	$\frac{N^{15}H_3}{N^{14}H_3}$	$\frac{N^{15}O}{N^{14}O}$	$\frac{HCN^{15}}{HCN^{14}}$	$\frac{CN^{15-}}{CN^{14-}}$	T, °K
Q_2/Q_1	1.1184	1.0908	1.0768	1.073_8	1.0736	1.0718	273.1
	1.1059	1.0814	1.0688	1.065_0	1.0655	1.0641	298.1
	1.0721	1.0558	1.0472	1.044_0	1.0439	1.0433	400
	1.0530	1.0410	1.0350	1.031_6	1.0316	1.0315	500
	1.0409	1.0311	1.0271	1.023_8	1.0238	1.0239	600
Isotopic exchange equilibrium constants							
$\frac{N^{15}H_4^+}{N^{14}H_4^+}$		∞	∞	∞	∞	∞	0
	1.000	1.025	1.039	1.042	1.042	1.043	273.1
	—	1.023	1.035	1.038	1.038	1.039	298.1
	—	1.015	1.024	1.027	1.027	1.028	400
	—	1.012	1.017	1.021	1.021	1.021	500
	—	1.010	1.013	1.017	1.017	1.017	600
$\left(\frac{N_2^{15}}{N_2^{14}}\right)^{1/2}$			∞	∞	∞	∞	0
	—	1.000	1.013	1.016	1.016	1.018	273.1
	—	—	1.012	1.015	1.015	1.016	298.1
	—	—	1.008	1.011	1.011	1.012	400
	—	—	1.006	1.009	1.009	1.009	500
	—	—	1.004	1.007	1.007	1.007	600
$\frac{N^{15}H_3}{N^{14}H_3}$				∞	∞	∞	0
	—	—	1.000	1.003	1.003	1.005	273.1
	—	—	—	1.003	1.003	1.004	298.1
	—	—	—	1.003	1.003	1.004	400
	—	—	—	1.003	1.003	1.003	500
	—	—	—	1.003	1.003	1.003	600
$\frac{N^{15}O}{N^{14}O}$					∞	∞	0
	—	—	—	1.000	1.000_2	1.002	273.1
	—	—	—	—	1.000_4	1.002	298.1
	—	—	—	—	1.000_1	1.001	400
	—	—	—	—	1.000_0	1.000	500
	—	—	—	—	1.000_0	1.000	600
$\frac{HCN^{15}}{HCN^{14}}$					∞	∞	0
	—	—	—	—	1.000	1.002	273.1
	—	—	—	—	—	1.001	298.1
	—	—	—	—	—	1.001	400
	—	—	—	—	—	1.000	500
	—	—	—	—	—	1.000	600

TABLE 2.

Ratios of the Vibrational Statistical Sums Q_2/Q_1 and Equilibrium Constants for the Isotopic Exchange of Oxygen and Its Compounds, after Grey [ ]

	$\left(\frac{CO_2^{18}}{CO_2^{16}}\right)^{1/2}$	$\frac{CO^{18}}{CO^{16}}$	$\left(\frac{CO_3^{18--}}{CO_3^{16--}}\right)^{1/3}$	$\left(\frac{SO_4^{18--}}{SO_4^{16--}}\right)^{1/4}$	$\left(\frac{SO_2^{18}}{SO_2^{16}}\right)^{1/2}$	$\frac{D_2O^{18}}{D_2O^{16}}$	$\left(\frac{O_2^{18}}{O_2^{16}}\right)^{1/2}$	$\frac{H_2O^{18}}{H_2O^{16}}$	$\left(\frac{ClO_2^{18}}{ClO_2^{16}}\right)^{1/2}$	T, °K
Q_2/Q_1	1.1331	1.1181	1.1090	1.1073	1.1017	1.0974	1.0923	1.0741	1.0717	273.1
	1.1172	1.1053	1.0945	1.0924	1.0888	1.0872	1.0818	1.0667	1.0621	298.1
	1.0750	1.0714	1.0576	1.0557	1.0551	1.0594	1.0533	1.0465	1.0375	400
	1.0525	1.0518	1.0388	1.0370	1.0376	1.0487	1.0374	1.0350	1.0251	500
	1.0387	1.0390	1.0279	1.0261	1.0271	1.0338	1.0274	1.0275	1.0179	600
				Isotopic exchange	equilibrium constants					
$\left(\frac{CO_2^{18}}{CO_2^{16}}\right)^{1/2}$		∞	∞	0	∞	∞	∞	∞	∞	0
	1.000	1.013	1.022	1.023	1.029	1.033	1.037	1.055	1.057	273.1
	—	1.011	1.021	1.023	1.026	1.028	1.033	1.047	1.052	298.1
	—	1.003	1.016	1.018	1.020	1.015	1.021	1.027	1.036	400
	—	1.000_7	1.013	1.015	1.014	1.008	1.016	1.017	1.027	500
	—	0.999_7	1.011	1.012	1.011	1.005	1.011	1.011	1.020	600
$\frac{CO^{18}}{CO^{16}}$			0	0	0	∞	∞	∞	∞	0
	—	1.000	1.008	1.010	1.015	1.019	1.024	1.041	1.043	273.1
	—	—	1.010	1.012	1.015	1.017	1.022	1.036	1.041	298.1
	—	—	1.013	1.015	1.015	1.011	1.017	1.024	1.033	400
	—	—	1.014	1.014	1.014	1.008	1.014	1.016	1.026	500
	—	—	1.011	1.013	1.012	1.005	1.011	1.011	1.021	600
$\left(\frac{CO_3^{18--}}{CO_3^{16--}}\right)^{1/3}$				0	∞	∞	∞	∞	∞	0
	—	—	1.000	1.002	1.007	1.011	1.015	1.033	1.035	273.1
	—	—	—	1.002	1.005	1.007	1.012	1.026	1.031	298.1
	—	—	—	1.002	1.002	0.998	1.004	1.011	1.019	400
	—	—	—	1.002	1.001	0.995	1.001	1.004	1.013	500
	—	—	—	1.002	1.001	0.994	1.000	1.000_4	1.010	600
$\left(\frac{SO_4^{18--}}{SO_4^{16--}}\right)^{1/4}$					∞	∞	∞	∞	∞	0
	—	—	—	1.000	1.005	1.009	1.014	1.031	1.033	273.1
	—	—	—	—	1.003	1.005	1.010	1.024	1.029	298.1
	—	—	—	—	1.001	0.997	1.002	1.009	1.018	400
	—	—	—	—	0.999	0.994	0.999_6	1.003	1.012	500
	—	—	—	—	0.999	0.993	0.999	0.999	1.008	600
$\left(\frac{SO_2^{18}}{SO_2^{16}}\right)^{1/2}$						∞	∞	∞	∞	0
	—	—	—	—	1.000	1.004	1.007	1.026	1.028	273.1
	—	—	—	—	—	1.001	1.006	1.021	1.025	298.1
	—	—	—	—	—	0.996	1.003	1.008	1.017	400
	—	—	—	—	—	0.994	1.000	1.003	1.012	500
	—	—	—	—	—	0.994	0.999_7	0.999_6	1.009	600

TABLE 2 (continued)

	$\left(\frac{CO_2^{18}}{CO_2^{16}}\right)^{1/2}$	$\frac{CO^{18}}{CO^{16}}$	$\left(\frac{CO_3^{18--}}{CO_3^{16--}}\right)^{1/3}$	$\left(\frac{SO_4^{18--}}{SO_4^{16--}}\right)^{1/4}$	$\left(\frac{SO_2^{18}}{SO_2^{16}}\right)^{1/2}$	$\frac{D_2O^{18}}{D_2O^{16}}$	$\left(\frac{O_2^{18}}{O_2^{16}}\right)^{1/2}$	$\frac{H_2O^{18}}{H_2O^{16}}$	$\left(\frac{ClO_2^{18}}{ClO_2^{16}}\right)^{1/2}$	T, °K
$\frac{D_2O^{18}}{D_2O^{16}}$							0	∞	∞	0
	—	—	—	—	—	1.000	1.005	1.022	1.024	273.1
	—	—	—	—	—	—	1.005	1.019	1.024	298.1
	—	—	—	—	—	—	1.006	1.013	1.021	400
	—	—	—	—	—	—	1.006	1.008	1.018	500
	—	—	—	—	—	—	1.006	1.006	1.015	600
$\left(\frac{O_2^{18}}{O_2^{16}}\right)^{1/2}$								∞	∞	0
	—	—	—	—	—	—	1.000	1.017	1.019	273.1
	—	—	—	—	—	—	—	1.014	1.019	298.1
	—	—	—	—	—	—	—	1.006	1.015	400
	—	—	—	—	—	—	—	1.002	1.012	500
	—	—	—	—	—	—	—	0.999_9	1.009	600
$\frac{H_2O^{18}}{H_2O^{16}}$									0	0
	—	—	—	—	—	—	—	1.000	1.002	273.1
	—	—	—	—	—	—	—	—	1.004	298.1
	—	—	—	—	—	—	—	—	1.009	400
	—	—	—	—	—	—	—	—	1.010	500
	—	—	—	—	—	—	—	—	1.009	600

TABLE 3

Ratios of the Statistical Sums Q_2/Q_1 and Equilibrium Constants for the Isotopic Exchange of Hydrogen and Its Compounds, after Urey [1]

	$\left(\frac{D_2O}{H_2O}\right)^{1/2}$	$\frac{DCl}{HCl}$	$\frac{DBr}{HBr}$	$\left(\frac{D_2}{H_2}\right)^{1/2}$	$\frac{DI}{HI}$	$\frac{LiD}{LiH}$	$\frac{NaD}{NaH}$	$\frac{KD}{KH}$	T, °K
Q_2/Q_1	16.467	6.3726	5.1278	4.2803	4.0172	1.8604	1.6908	1.5047	273.1
	12.518	5.3059	4.3454	3.7346	3.4744	1.7287	1.5819	1.4248	298.1
	5.8504	3.1881	2.7445	2.5570	2.3236	1.4151	1.3271	1.2377	400
	3.7648	2.3695	2.1013	2.0462	1.8434	1.2700	1.2105	1.1524	500
	2.8222	1.9403	1.7652	1.7650	1.5873	1.1891	1.1463	1.1055	600

Isotopic exchange equilibrium constants

		∞	∞	∞	∞	∞	∞	∞	0
$\left(\frac{D_2O}{H_2O}\right)^{1/2}$	1.000	2.584	3.211	3.847	4.099	8.851	9.739	10.944	273.1
	—	2.359	2.881	3.352	3.603	7.241	7.913	8.786	298.1
	—	1.835	2.132	2.288	2.518	4.134	4.408	4.727	400
	—	1.589	1.792	1.840	2.042	2.964	3.110	3.267	500
	—	1.448	1.599	1.599	1.778	2.373	2.462	2.533	600
			∞	∞	∞	∞	∞	∞	0
$\frac{DCl}{HCl}$	—	1.000	1.243	1.489	1.586	3.425	3.769	4.235	273.1
	—	—	1.221	1.421	1.527	3.069	3.354	3.724	298.1
	—	—	1.162	1.247	1.372	2.253	2.403	2.576	400
	—	—	1.128	1.158	1.285	1.866	1.957	2.056	500
	—	—	1.104	1.104	1.228	1.639	1.701	1.763	600
				∞	∞	∞	∞	∞	0
$\frac{DBr}{HBr}$	—	—	1.000	1.198	1.276	2.756	3.033	3.408	273.1
	—	—	—	1.164	1.251	2.514	2.747	3.050	298.1
	—	—	—	1.073	1.181	1.939	2.068	2.217	400
	—	—	—	1.027	1.140	1.655	1.736	1.823	500
	—	—	—	1.000	1.112	1.484	1.540	1.597	600
					0	∞	∞	∞	0
$\left(\frac{D_2}{H_2}\right)^{1/2}$	—	—	—	1.000	1.065	2.301	2.532	2.845	273.1
	—	—	—	—	1.075	2.160	2.361	2.621	298.1
	—	—	—	—	1.100	1.807	1.927	2.066	400
	—	—	—	—	1.110	1.611	1.690	1.776	500
	—	—	—	—	1.112	1.484	1.540	1.597	600

TABLE 3 (continued)

	$\left(\frac{D_2O}{H_2O}\right)^{1/2}$	$\frac{DCl}{HCl}$	$\frac{DBr}{HBr}$	$\left(\frac{D_2}{H_2}\right)^{1/2}$	$\frac{DI}{HI}$	$\frac{LiD}{LiH}$	$\frac{NaD}{NaH}$	$\frac{KD}{KH}$	T°, K
						∞	∞	∞	0
$\frac{DI}{HI}$	—	—	—	—	1.000	2.159	2.376	2.670	273.1
	—	—	—	—	—	2.010	2.196	2.439	298.1
	—	—	—	—	—	1.642	1.751	1.877	400
	—	—	—	—	—	1.451	1.523	1.600	500
	—	—	—	—	—	1.335	1.385	1.436	600
							∞	∞	0
$\frac{LiD}{LiH}$	—	—	—	—	—	1.000	1.100	1.236	273.1
	—	—	—	—	—	—	1.093	1.213	298.1
	—	—	—	—	—	—	1.066	1.143	400
	—	—	—	—	—	—	1.049	1.102	500
	—	—	—	—	—	—	1.038	1.076	600
								∞	0
$\frac{NaD}{NaH}$	—	—	—	—	—	—	1.000	1.124	273.1
	—	—	—	—	—	—	—	1.110	298.1
	—	—	—	—	—	—	—	1.072	400
	—	—	—	—	—	—	—	1.050	500
	—	—	—	—	—	—	—	1.038	600

Equilibrium Constants for Isotopic Exchange of Tritium Halides, after Zeise [2].

TABLE 4a

Theoretical Values of Equilibrium Constants for Exchange Reactions (1) and Dissociation (2) of Tritium Halides.

$$(1)\ HX + TX \rightleftarrows HT + X_2$$
$$(2)\ 2TX \rightleftarrows T_2 + X_2;\ X = F, Cl, Br, I$$

T, °K	X = F		X = Cl		X = Br		X = I	
	-log K (1)	-log K (2)	-log K (1)	-log K (2)	log K (1)	-log K (2)	-log K (1)	-log K (2)
1500	19,040	19 400	6.9205	7.2182	4.1105	4.3921	0.881	1.147
1400	20.406	20.774	7.3958	7.6936	4.3797	4.6592	0.912	1.174
1300	21.981	22.358	7.9430	8.2414	4.6889	4.9662	0.948	1.206
1200	23.818	24 205	8,5811	8.8792	5.0504	5.3251	0.991	1.243
1100	25.987	26 387	9.3346	9.6334	5.4784	5.7504	1.043	1.288
1000	28 587	29.003	10.2373	10 5374	5,9901	6.2592	1.104	1.341
900	31.762	32.197	11.3410	11.6431	6.6160	6.8810	1.180	1.409
800	35.728	36.188	12.7175	13.0228	7.3969	7.6601	1.273	1.492
700	40 823	41.324	14.4843	14.7960	8.3974	8.6584	1.391	1.599
600	47.609	48.142	16.8348	17.1571	9.7278	9.9882	1.547	1.742
500	57,109	57.692	20.1153	20.4520	11.583	11.846	1.760	1.942
400	71,322	72.005	25.0202	25.3829	14.350	14.619	2.066	2.232
300	95.007	95.841	33.1789	33.5869	18.943	19.228	2.545	2.691
298.16	95.593	96.430	33 3796	33,7888	19.052	19.337	2.558	2.703

TABLE 4b

Theoretical Values of Equilibrium Constants for Isotopic Exchange Between Tritium Halides and Protium Halides, for example HF + TI ⇄ TF + HI

T, °K	$K=\frac{(TF)(HI)}{(HF)(TI)}$	$\frac{(TF)(HBr)}{(HF)(TBr)}$	$\frac{(TF)(HCl)}{(HF)(TCl)}$	$\frac{(TCl)(HI)}{(HCl)(TI)}$	$\frac{(TCl)(HBr)}{(HCl)(TBr)}$	$\frac{(TBr)(HI)}{(HBr)(TI)}$
2000	1.1408	1.1175	1.0928	1.0440	1 0226	1.0209
1500	1.2440	1.1999	1.1565	1.0756	1,0375	1.0367
1400	1.2770	1.2263	1.1760	1.0859	1.0427	1.0414
1300	1.3174	1.2577	1.1984	1,0993	1.0495	1,0474
1200	1 3669	1.2961	2.2282	1.1129	1.0553	1.0546
1100	1.4281	1.3429	1.2625	1.1312	1.0636	1.0635
1000	1 5060	1.4013	1.3037	1.1543	1.0740	1.0747
900	1.6056	1.4749	1.3571	1.1832	1.0869	1.0886
800	1.7378	1.5707	1.4254	1.2192	1.1019	1.1064
700	1.9187	1.6980	1.5113	1.2696	1.1235	1.1300
600	2.1785	1,8758	1.6263	1.3396	1.1534	1.1614
500	2.5812	2.1422	1.8055	1.4296	1.1865	1.2049
400	3 2915	2 5930	2.0920	1.5734	1.2395	1.2694
300	4.8724	3.5346	2.6617	1.8305	1.3279	1.3785
298.16	4.9205	3.5619	2.6778	1.8375	1.3301	1.3814
273.16	5.6780	3.9895	2.9253	1.9410	1.3638	1.4232

TABLE 4c

Theoretical Values of Equilibrium Constants for Isotopic Exchange Between H_2 and Tritium Halides $H_2 + TX \rightleftarrows HT + HX$; where X = F, Cl, Br, I

T, ° K	$K=\frac{(HT)(HF)}{(H_2)(TF)}$	$\frac{(HT)(HCl)}{(H_2)(TCl)}$	$\frac{(HT)(HBr)}{(H_2)(TBr)}$	$\frac{(HT)(HI)}{(H_2)(TI)}$	$\frac{Q_{HT}}{Q_{H_2}}$
2000	1.9031	1.9995	2.0447	2.0874	2 2344
1500	1.7162	1.9848	2.0593	1.1349	2 4084
1400	1.6817	1.9777	2.0622	2.1476	2 4652
1300	1.6404	1.9259	2.0632	2 1610	2.5338
1200	1.5914	1.9546	2 0627	2 1753	2.6184
1100	1.5331	1.9356	2.0588	2 1895	2 7244
1000	1.4633	1.9092	2.0505	2.2037	2 8600
900	1.3702	1,8717	2 0343	2.2145	3 0372
800	1.2776	1.8211	2.0067	2 2203	3.2776
700	1 1547	1.7452	1.9608	2.2156	3 6172
600	1.0064	1.6367	1.8876	2 1925	4.1282
500	0.82820	1.4953	1.7742	2.1378	4.9682
400	0.61718	1.2912	1.6003	2.0215	6.5606
300	0.37767	1.0053	1,5349	1.8402	10 426
298.16	0.37311	0.99912	1,3290	1.8359	10.547
273.16	0.31135	0.91080	1 2421	1.7678	12.511

TABLE 4d

Theoretical Values of Equilibrium Constants for Isotopic Exchange Between H_2 and Two Molecules of a Tritium Halide $H_2 + 2TX \rightleftarrows T_2 + 2HX$; where X = F, Cl, Br, I

T, ° K	$K=\frac{(T_2)}{(H_2)}\left(\frac{HF}{TF}\right)^2$	$\frac{(T_2)}{(H_2)}\left(\frac{HCl}{TCl}\right)^2$	$\frac{(T_2)}{(H_2)}\left(\frac{HBr}{TBr}\right)^2$	$\frac{(T_2)}{(H_2)}\left(\frac{HI}{TI}\right)^2$	$\frac{Q_{T_2}}{Q_{H_2}}$
2000	0.91077	1.0054	1.0513	1.0957	1 2555
1500	0.74773	1.0001	1.0766	1.1571	1 4725
1400	0.72037	0.99627	1.0833	1.1748	1.5480
1300	0.68870	0.98904	1.0894	1.1952	1 6431
1200	0.65223	0,98390	0.0957	1.2186	1 7656
1100	0.61032	0.97279	1.1006	1.2447	1.9272
1000	0.56205	0.95682	1.1036	1.2748	2 1471
900	0.50693	0.93354	1.1028	1.3069	2 4582
800	0.44377	0.90161	1.0948	1.3402	2.9206
700	0.37282	0.85154	1.0749	1.3725	3 6583
600	0.29460	0.77916	1.0366	1.3982	4 9570
500	2.21122	0.68857	0.96932	1.4074	7 6011
400	0.12797	0.56009	0.86047	1.3865	14 461
300	0.055452	0.39285	0.69279	1.3164	42 263
298.16	0.054294	0.38935	0.68884	1.3145	43 385
273.16	0.039897	0.34141	0.63496	1.2863	64 417

TABLE 4e

Theoretical Values of Equilibrium Constants for Isotopic Exchange Between Water and Tritium Halides (as ideal gases) $H_2O + TX \rightleftarrows HTO + HX$, where X = F, Cl, Br, I

T, °K	$K=\frac{(T_2O)}{(H_2O)}\left(\frac{HF}{TF}\right)^2$	$\frac{(T_2O)}{(H_2O)}\left(\frac{HCl}{TCl}\right)^2$	$\frac{(T_2O)}{(H_2O)}\left(\frac{HBr}{TBr}\right)^2$	$\frac{(T_2O)}{(H_2O)}\left(\frac{HI}{TI}\right)$	$\frac{Q_{T_2O}}{Q_{H_2O}}$
2000	0.97586	1.1654	1.2186	1.2701	1.4553
1500	0.96902	1.2961	1.3953	1.4995	1.9083
1400	0.96859	1.3396	1.4565	1.5796	2.0814
1300	0.96814	1.3904	1.5315	1.6801	2.3098
1200	0.96834	1.4607	1.6267	1.8092	2.6213
1100	0 90991	1.5460	1.7490	1.9781	3.0627
1000	0.97335	1.6570	1.9112	1.2076	3.7183
900	0.98047	1.8057	2.1331	2.5276	4.7545
800	0.99274	2.0169	2.4491	2.9981	6.5335
700	1.0145	2.3171	2.9250	3.7347	9.9546
600	1.0526	2 7839	3.7036	4.9956	17.711
500	1.1228	3 6601	5.1525	7.4808	40.404
400	1.2548	5.4917	8.4369	13,594	141.79
300	1 5477	10.965	19.336	36,743	1179.6
298,16	1,5559	11.158	19.740	37.671	1243.3
273,16	1 6867	14.433	26.844	54.377	2723.3

TABLE 4f

Theoretical Values of Equilibrium Constants for Isotopic Exchange Between One Water Molecule and Two Molecules of a Tritium Halide (as ideal gases) $H_2O + 2TX \rightleftarrows T_2O + 2HX$, where X = F, Cl, Br, I

T, °K	$K=\frac{(HTO)\,(HF)}{(H_2O)\,(TF)}$	$\frac{(HTO)\,(HCl)}{(H_2O)\,(TCl)}$	$\frac{(HTO)\,(HBr)}{(H_2O)\,(TBr)}$	$\frac{(HTO)\,(HI)}{(H_2O)\,(TI)}$	$\frac{Q_{HTO}}{Q_{H_2O}}$
2000	1.9638	2.1460	2.1945	2.2405	2.3982
1500	1.9531	2.2588	2.3436	2.4296	2.7408
1400	1.9512	2.2946	2.3927	2.4917	2.8602
1300	1.9492	2.3359	2.4516	2.5678	3.0108
1200	1.9475	2.3919	2.5242	2.6620	3 2042
1100	1.9471	2.4583	2.6147	2.7807	3.4600
1000	1.9477	2.5413	2.7293	2.9333	3.8068
900	1.9513	2.6481	2.8781	3.1331	4.2970
800	1.9587	2.7619	3.0765	3.4039	5.0248
700	1.9732	2.9821	3.3505	3.7860	6.1810
600	1.9995	3.2517	3.7506	4.3559	8.2018
500	2.0491	3.6996	4.3895	5.2892	12,292
400	2.1334	4.4631	5.5319	7.0221	22.678
300	2.3024	6.1282	8.1380	11.218	63.562
298,16	2 3067	6.1772	8.2163	11.350	65.206
273,16	2.3743	6.9455	9.4722	13.481	95.404

Equilibrium Constants for the Isotopic Exchange Reaction $C^{14}O/COCl_2$ after Stranks [3]

TABLE 5a

Theoretical Equilibrium Constants for the Isotopic Exchange of $C^{14}O/COCl_2$, after Stranks

T, °K	f_{COCl}	f_{CO}	K
273.16	1.3465	1.2155	1.1078
283.16	1.3263	1.2052	1.1005
293.16	1.3083	1.1959	1.0940
303.16	1.2915	1.1871	1.0879
313.16	1.2762	1.1791	1.0824
323.16	1.2621	1.1715	1.0773
333.16	1.2492	1.1645	1.0727
373.16	1.2061	1.1405	1.0575
473.16	1.1408	1.0996	1.0375
573 16	1.0983	1.0774	1.0222
673.16	1.0737	1 0575	1.0153
723.16	1.0647	1.0506	1 0134
773.16	1.0545	1.0456	1.0085

TABLE 5b

Experimental and Theoretical Equilibrium Constants for the Isotopic Exchange of $C^{14}O/COCl_2$, after Stranks

T, °C	K_{expt}*	$K_{theoret}$
10.00	1.10565	1.1005
20.00	1.09865	1.0940
30.00	1.0886	1.0879
40.00	1.08315	1.0824
50.00	1.07745	1.0773
60.00	1.07265	1.0727
100.00	1.05665	1 0575
200.00	1.0368	1.0375
300.00	1.0222	1.0222
400.00	1.01235	1.0153
450.00	1.00555	1.0134
500.00	1.00195	1.0085

---

* Average values of K_{expt} calculated by two methods are given. The fifth figure is the result of averaging.

LITERATURE CITED

[1] H. Urey, Isotope Chemistry I, Moscow, Foreign Lit. Press (1948), p. 86.

[2] H. Zeise, Thermodynamik. B. III/1 (1954).

[3] D.R. Stranks, Trans. Far. Soc. 51, No. 4, 499 (1955).

III. TABLES OF KINETIC ISOTOPE EFFECTS AND OF ISOTOPIC EXCHANGE KINETICS

TABLE 1

Maximum Possible Values of the Isotope Effects Caused by Changes of Zero-point Vibration Energies of Different Bonds on Replacement of H by D, as Functions of the Temperature, after Wiberg [1]

Bond	E_0, cal/mole	T, °C	K_H/K_D	Bond	E_0, cal/mole	T, °C	K_H/K_D	Bond	E_0, cal/mole	T, °C	K_H/K_D
C—H	~1150	0	8.3	N—H	~1270	0	10.3	O—H	~1400	0	12.6
		25	6.9			25	8.5			25	10.6
		100	4.7			100	5 5			100	6.6
		200	3.4			200	3.9			200	4.4
		300	2 7			300	3.0			300	3.4
		500	2 1			500	2.2			500	2.5

TABLE 2

Isotope Effects on Neutralization of the Carbonium Ion in Reactions of Metalloorganic Compounds with Methyl Alcohol, after Wiberg [1] $RMgBr + CH_3OH \longrightarrow RH + BrMgOCH_3$.

Compound	K_{CH_3OH}/K_{CH_3OD}	Compound	K_{CH_3OH}/K_{CH_3OD}
1-Butylmagnesium bromide	0.84	Phenyllithium	0.90
1-Butyllithium	1.00	Benzylmagnesium chloride	0.96
Phenylmagnesium bromide	0.97	Methylsodium propionate	1.16

TABLE 3

Isotope Effects in Reactions Catalyzed by Enzymes, after Wiberg [1].

Reaction	Enzyme	K_{D_2O}/K_{H_2O}	Michaelis constant
Hydrolysis of salicin	Emulsion	0.60	0.017-0.045
Hydrolysis of phenyl glucoside	"	0.74	0.04 -0.065
Hydrolysis of p-cresyl glucoside	"	0.85	0.14
Hydrolysis of n-butyl glucoside	"	1.04	0.22
Hydrolysis of methyl glucoside	"	1.27	0.62 -1.12
Hydrolysis of salicin	"	1.26	—
Inversion of sucrose	Invertase	0.76	—
Fermentation of glucose	—	0.46	—
Fermentation of sucrose	—	0.50	—

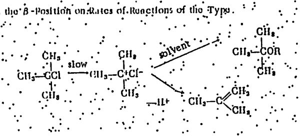
TABLE 4

Effect of Replacement of Protium by Deuterium on the Rates of Enolization Reactions, after Wiberg [1]

Reaction	Solvent	Reagent	T, °C	K_H/K_D
Bromination of nitromethane-d_3	H_2O	CH_3COO^-	25	6 53
	H_2O	$ClCH_2COO^-$	25	4.28
	H_2O	H_2O	70	3.78
	D_2O	CH_3COO^-	25	6.92
	D_2O	$ClCH_2COO^-$	25	5.18
	D_2O	H_2O	70	5 14
Enolization of nitroethane-d_1	D_2O	HO^-	5	5.5
Enolization of nitroethane-d_2	D_2O	HO^-	0	10
Bromination of acetone-d_6	H_2O	H_3O^+	25	7 7
	D_2O	H_3O^+	25	7.7
	H_2O	RCOOH	25	~7 7
	H_2O	CH_3COO^-	25	~7
Racemization of phenyl-p-tolyl acetic-d acid	H_2O	OH^-	100	4 6

TABLE 5

Effect of Deuterium in the β-Position on Rates of Reactions of the Type



After Wiberg [1]

Compound	Solvent	Relative olefin fraction*	T, °C	K_H/K_D
2-Methyl-2-butyl-3d$_2$ chloride	Anhydrous ethanol	0.25/0.36	25	1.40
2-Methyl-d$_3$-2-butyl-1-d$_3$-chloride	"	0.37/0.36	25	1.78
2-Methyl-d$_3$-2-butyl-1,3-d$_5$ chloride	"	0.23/0.36	25	2.35
2,3-Dimethyl-2-butyl-3-d$_1$-chloride	"	0.63/0.66	25	1.28
2-Pentyl-1,3-d$_5$-chlorosulfite	Dioxane		77.5	1.41
	isooctane		95.5	3.34
2-Pentyl-1,3-d$_5$ bromide	HCO_3H		98	1.39
2-Pentyl-1,3-d$_5$ tolylsulfonate	CH_3COOH HCOOH		78.4	1.57
	Anhydrous		39.9	1.69
	ethanol		58.2	1.40
1-(p-Methyl-d$_3$-phenyl)ethyl chloride	CH_3COOH		50	1.10
1-p-Tolylethyl-2d$_3$-chloride	CH_3COOH		50	1.28

TABLE 6

Isotope Effects in Replacement of Protium by Deuterium and Tritium in Certain Oxidation and Reduction Reactions of Organic Compounds, after Wiberg [1]

Reaction	Solvent	Reagent	T, °C	KH/KD
Oxidation of 2-propanol-2d$_1$	H_2O	$HCrO_4^-$	25	6.7
	Anhydrous CH_3COOH	$HCrO_4^-$	0	8.2
	"	$ClCrO_3^-$	0	9.6
Decomposition of diisopropyl-d, chromate	Benzene		25	4.6
Oxidation of ethanol-1-t$_1$	H_2O	Br_2	37.5	6.7
Oxidation of benzyl alcohol-α-t$_1$	H_2O	$HCrO_4^-$	37.5	5
Oxidation of benzohydrol-α-d	H_2O	MnO_4^-, OH^-	25	6.6
Oxidation of benzaldehyde-d$_1$	Anhydrous CH_3COOH	$HCrO_4^-$	25	4.3
	H_2O	MnO_4^- at pH 7	25	7.5
	H_2O	MnO_4^- at pH 13	25	2.7
Oxidation of p-chlorobenzaldehyde	H_2O	MnO_4^- at pH 7	25	7.4
	H_2O	MnO_4^- at pH 13	25	1.9
Oxidation of piperonal-d$_1$	H_2O	MnO_4^- at pH 8	25	4.1
	H_2O	MnO_4^- at pH 13	25	3.9
	H_2O	MnO_4^- at pH 13	25	3.3
Oxidation of formate-d$_1$ ion	H_2O	MnO_4^-	25	7.4
Cannizzaro reaction for benzaldehyde-d$_1$	Anhydrous ethanol	OH^-	100	1.8
Cannizzaro reaction for benzaldehyde-t$_1$	Anhydrous methanol	OH^-	98	1.24
Reduction of o- and m-nitrobenzenediazonium ion:				
by ethanol-1-t$_1$	Ethanol			7
by methanol-1-t$_1$	Methanol			7

TABLE 7

Isotope Effects in Reactions of Organic Compounds with Free Atoms and Radicals; after Wiberg [1]

Compound	Radical	T °C	K_H/K_D
Toluene-α-d$_1$	Cl	80	2 2
	Cl	80	2 0
	Br	80	3.3
	Br	77	4 6
	N-succinimidyl	77	4.9
	CH_3COO	120	9.9
Toluene-α-d$_2$	Cl	77	1.5
	Br	77	4.9
	N-succinimidyl	77	5.0
Ethylbenzene-α-d$_1$	Cl	80	1.4
	Br	80	2.4
	$(CH_3)_3CO$	120	4.1
	CH_3COO	120	6 5
Cyclohexane-α$_1$	Cl	80	1.4
	Br	80	2.4
	CH_3COO	120	6.9
2-Propanol-2-d$_1$	CH_3COO	120	6.3
Diphenylmethane-α-d$_1$	CH_3COO	120	6.7
Acetic-α-d$_1$ acid	CH_3COO	120	8 3
Propionic-α-d$_1$ acid	CH_3COO	120	6 8
Isobutyric-α-d$_1$ acid	CH_3COO	120	5.3
Isobutyryl-α-d$_1$ chloride	CH_3COO	100	1.4
2-Methylpropane-2-d$_1$	Cl	—15	4 8

TABLE 8

Kinetic Isotopic Exchange Constants for Electron Transfer Reactions, after Zwolinski, Marcus and Eyring [2]

Reactions of the 1st class; cations.

Reaction	ΔE, kcal/mole	ΔS, kcal/mole	Method of isolation or detection	Solvent	μ	ΔF_{obs}, kcal/mole	ΔF_{calc}, kcal/mole
$Co(en)_3^{2+} - Co(en)_3^{3+}$ *	14.3	—33.	Extraction	HCl	1.0	23.5	16.8
$Co(NH_3)_6^{2+} - Co(NH_3)_6^{3+}$	Slow		»	HCl	—	—	—
$Fe^{2+} - Fe^{3+}$	9.9	—25	Precipitation	$HClO_4$	0.55	16.7	16.7
$Fe^{2+} - FeOH^{2+}$	7.4	—18	»	$HClO_4$	0.55	12.2	13.1
$Fe^{2+} - FeCl^{2+}$	8.8	—24	»	$HClO_4$	0.55	15.3	15.1
$Fe^{2+} - FeCl_2^{+}$	9.7	—20	»	$HClO_4$	0.55	15.1	13.1
$Fe^{2+} - FeF_2^{+}$	9.1	—20	»	$HClO_4$	0.5	14.2	15.1
$Fe^{2+} - FeF^{2+}$	9.5	—22	»	$HClO_4$	0.5	14.9	13.1
$Ce^{3+} - Ce^{4+}$	7.7	—40	Extraction	HNO_3	6.18	18.0	19.1
$Ce^{3+} - Ce^{4+} \cdot [H^+]^{2-}$	24.0	+25	"	HNO_3	6.18	16.6	
$NpO_2^{+} - NpO_2^{2+}$	8.3	—24		$HClO_4$	1.0	14.3	14.6
$VOH^{2+} - VO_2^{2+}$	10.7	—24	Ion exchange	$HClO_4$	2.5	17.2	16.0
$Os(bipy)_3^{2+} - Os(bipy)_3^{3+}$ **	Rapid.		Optical activity	$HClO_4$	—	—	—

* (en) ethylenediamine
** (bipy) bipyridyl

Reactions of the 1st class; anion.

Reaction	Rate constant	Method of isolation	Solvent	T, °C
$MnO_4^{2-} - MnO_4^{-}$	$k' = 650$ mole/liter·sec	Extraction	9.15 M NaOH	1
$Fe(CN)_6^{4-} - Fe(CN)_6^{3-}$	$k' \approx 10^3$ mole/liter·sec	Precipitation	H_2O	4
$Mo(CN)_8^{4-} - Mo(CN)_8^{3-}$	Complete in 5 min	»	0.01 M NH_4ClO_4	2

Reactions of the 2nd class.

Reaction	ΔE, kcal/mole	ΔS, kcal/mole	Method of isolation	Solvent	μ	ΔF_{obs}	Order with respect to other substances
$Tl^{+} - TlOH^{2+}$	14.7	—33	Precipitation	$HClO_4$	6.0	23.9	—
$Sn^{2+} - Sn^{4+}$	10.8	—34	»	HCl	10.0	23.3	—
$SnCl_2 - SnCl_4$	23.7	—16	»	Abs. alcohol	—	18.3	—
$Sb^{3+} - Sb^{5+}$	27.0	—32	»	HCl	6—12	35.9	$(H^+)^4 (Cl^-)^9$
$Eu^{2+} - Eu^{3+}$	20.8	—1.3	»	HCl	2.0	21.0	(Cl^-)
$U^{4+} - U^{6+}$	33.4	+31	»	HCl	>1	23.6	$(H^+)^3$

LITERATURE CITED

[1] K.B. Wiberg, Chem. Rev. 55, No. 4, 713 (1955).

[2] B.J. Zwolinski, R.J. Marcus and H. Eyring, Chem. Rev. 55, No. 1, 157 (1955).

CONVENTIONAL SIGNS

A – central atom in complex ion (213)
A – acid (154, 180, 183, 267-270, 274-275)
a – activity coefficient (54, 105, 109, 210)
a – initial concentration (96, 119-120, 248, 337-338, 341, 342)
a – constant (49-50)
a – constant in Equation (164), Chapter I (68, 70)
a_0 – Bohr radius
a (x) – catalyst activity in dynamic conditions as a function of the distance along the layer (107, 108, 109)
B – base (180, 183, 260, 267-270, 274-275)
B – rotational spectrum structure constant (59, 60)
B_0 – rotational spectrum structure constant at $v = 0$ (26, 59, 76)
B_e – rotational spectrum structure constant at low vibration amplitudes (76)
$B_v = [B_0(1 - \alpha v)]$, where α is a constant (25, 26)
b – constant in Equation (127a) Chapter I; ratio of the separation coefficients in adsorption (50)
b – constant in Equation (164), Chapter I (70)
b – initial concentration (96, 119-120, 248)
b – number of rapidly exchanging atoms in molecule (314-316)
C – constant in integration limits of Equation (60), Chapter V (333)
c – concentration for isochrone (332, 333)
c – heat capacity (14, 92)
c – velocity of light (17, 23, 24, 37, 38, 233, 245, 251)
D – energy of dissociation (43, 50, 145, 192, 269)
D – diffusion coefficient (106, 198, 262)
D_v – rotational constant (25, 26)
D_0 – rotational constant (26)
D_e – rotational constant (76)
D = D(t) – specific content of deuterium at time t (90, 124)
D_0 – specific content of deuterium at the initial moment (90, 124)
d – number of slowly exchanging atoms in the molecule (314, 316)
E – internal energy, of a single molecule or of a gram-molecule (14, 15, 16, 23, 35, 91, 131, 313)
E – activation energy
E_0 – zero-point energy
Et – ethyl
F – free energy (14, 15, 37, 53, 71)
F – relative exchange, exchange fraction
f – activity coefficient (121)
f – separation coefficient (34-40, 43, 48-50, 65, 70)
f – conversion fraction (254, 290, 338-342, 365)
G – Bigeleisen function
g – statistical weight
H – enthalpy
h – Planck constant
Hal – halogen
I – moment of inertia (Chapter I)

J – rotational quantum number
K_{diss} – dissociation constant
K – equilibrium constant
k – rate constant
k – Boltzmann constant (Chapter I, 87, 134, 232-235, 244-245)
l – constant with the dimensions of energy (110)
l – distance (105-106, 111)
M – atomic weight (30, 31, 32, 33)
M – molecular weight (17, 38, 279, 280)
M – extraneous molecule which removes energy in a triple collision (286, 288, 289, 367)
m – particle mass
$\bar{m}$ – effective mass of intermediate complex (232-235, 237, 238, 242)
Me – metal
Me – methyl group (176-181)
N – Avogadro number (15, 17, 30, 37, 54, 55)
N – number of active centers (106-108, 109, 110)
n – number of atoms (14, 26, 38, 56)
n – number of molecules (135, 279)
n – principal quantum number (17, 135)
p – force constant (23, 24, 43, 44, 49-50, 269)
p – pressure (15, 17, 130, 287, 350)
p – equilibrium vapor pressure (54, 55, 80)
p – saturated vapor pressure (51-53)
p – partial pressure (62, 113, 114, 125, 142)
Ph – C_6H_5-group
Q – statistical sum (33-36, 40-42, 67, 75, 233, tables in Appendix)
Q – heat effect
Q_0 – heat effect at 0°K
R – gas constant (Chapter I, 88, 93, 109-110, 134-135, 164, 191, 212, 313-314, 330-333)
R – monoradical
IR – biradical
R° – negatively charged monoradical (268-270, 271)
R – isotopic exchange rate
R – distance between nuclei in molecule (23, 24, 131-132, 134, 135)
r – atomic radius (20, 28)
r – apparent isotopic exchange rate constant
S – entropy
S – substrate (267-270)
S – separation coefficient (290, 339, 340, 342)
s – stream cross section (106, 111, 117)
T – temperature in °K
t – time
t – tritium (272, 277)
$t_{1/2}$ – half-exchange time
U – potential energy
u – reduced energy of fundamental vibrations
u – linear flow rate (105-108, 110)
V – volume
v – vibrational quantum number (Chapter I)
v – volume flow rate (Chapter II)
w – reaction rate
x – concentration (90, 91, 248)
x – distance in direction of flow (Chapter III)
Z – statistical sum
Z^0 – statistical sum from zero-point level

α – kinetic isotope coefficient
α – radioactivity (203, 365)
α – distribution coefficient (68, 70)
α – structural position (Chapter V)
α – reaction order (Chapter II, 205)
α – constant (131, 216)
β – factor representing degree of nonequivalence (68, 70, 71)
β – fractional exponent in statistical kinetic equations for heterogeneous surfaces (256, 294)
β – reaction order (Chapter II, 205)
β – structural position (Chapter V)
γ – constant (38, 40)
γ – molar fraction (53, 55, 172)
γ – thermodynamic isotopic correction (249, 250, 264)
γ – structural position (314, 315)
δ – kinetic isotopic coefficient
δ – correction term (36, 37, 43)
δ – steric factor (164, 189)
δ – width of energy barrier at the upper part (232, 233, 235)
θ – degree of cover
κ – conversion coefficient
μ_a – reduced mass in atomic weight units, equal to $\frac{m_1 \cdot m_2}{m_1 + m_2} \cdot N$ (44, 49, 50)
ν – frequency (sec^{-1})
ν – stoichiometric coefficients (16, 38-39, 40, 95-96, 97, 285)
Π – product
ρ – specific radioactivity (246, 248, 252, 254, 376)
ρ – specific contents of isotopes
τ – symmetry factor
τ – average life (230, 232, 233, 373)
τ – contact time (105, 110, 111)
$\tau_{1/2}$ – half-life
$\tau_{1/2}$ – half-exchange time (118, 124-125, 130, 139)
Φ – thermodynamic potential
Ω – distribution function
ω – characteristic frequency (cm^{-1})
* – tagging sign
$\neq$ – sign of intermediate state

CONVENTIONAL SIGNS IN TABLES IN THE APPENDIX

E^0, F^0, H^0, S^0 and Φ^0 – corresponding thermodynamic functions in the standard state
A, δ, ρ – constants in approximate equations used for calculation of statistical sums and rotational energies (see Refs. [4] and [5] on page 432)
S – symmetry number
d – deuterium
t – tritium

INDEX OF ISOTOPES MENTIONED IN THE TEXT, AND THEIR PROPERTIES*

[illegible] Isomeric nucleus
E electron capture
I– isomeric conversion
D– spontaneous fission of nucleus into two fragments

Element	Isotope	Abundance, in %	Half-life	Radiation and its energy, Mev
Hydrogen	H^1 H^2 (D)	99.98 0.02		— —
	H^3 (T)		12.5 years	β^- 0.0179
Helium	He^3 He^4			— —
Lithium	Li^6 Li^7	7.3 92.7		— —
Beryllium	Be^7 Be^9	 100	52.9 days —	E, γ 0.453 —
	Be^{10}		$2.5 \cdot 10^6$ years	β^- 0.566
Boron	B^{10} B^{11}	18.83 81.17		— —
Carbon	C^{11}		20.42 min.	β^+ 1
	C^{12} C^{13}	98.9 1.1		— —
	C^{14}		5700 years	β^- 0.155
Nitrogen	N^{13}		9.93 min.	β^+ 1.218
	N^{14} N^{15}	99.62 0.38		— —
	N^{16}		7.35 sec	β^- 3.8 γ 6.5

(Continued)

Element	Isotope	Abundance, in %	Half-life	Radiation and its energy, Mev
Oxygen	O^{16} O^{17} O^{18}	99.7575 0.0392 0.2033		— — —
Fluorine	F^{18} F^{19}	 100	107 min.	β^+ 0.635
Neon	Ne^{20} Ne^{22}	90.51 9.21		— —
Sodium	Na^{22}		2.6 years	β^+ 0.575, γ 1.277
	Na^{23}	100		
	Na^{24}		15 hours	β^- 1.390 γ 1.380; 2.76
Magnesium	Mg^{24} Mg^{26} Mg^{27}	78.6 11.29 	 10.2 min.	— — β^- 0.79; 1.80 γ 0.84
Silicon	Si^{28} Si^{30}	92.16 3.13		— —
Phosphorus	P^{31}	100		—
	P^{32}		14.07 days	β^- 1.689
Sulfur	S^{32} S^{33} S^{34}	95.06 0.74 4.18		— — —
	S^{35}		87.1 days	β^- 0.170
	S^{36}	0.014		
Chlorine	Cl^{35} Cl^{36} Cl^{37} Cl^{38}	75.43 24.57 	 $0.44 \cdot 10^6$ years 38.5 min.	— β^- 0.713 — β^- 1.11; 2.77; 4.81 γ 1.65; 2.15
Argon	A^{36} A^{40}	0.307 99.632		— —
Potassium	K^{39} K^{41}	93.306 6.683		— —
Calcium	Ca^{40} Ca^{45}	96.92 	 152 days	— β^- 0.26

---

* Selinov, Atomic Nuclei and Nuclear Transformations, Moscow–Leningrad, State Tech. Press (1951).

(Continued)

Element	Isotope	Abundance, in %.	Half-life	Radiation and its energy, Mev
Iron	Fe^{55}		≈ 4 years	
Bromine	Br^{77}		57.2 hours	β^+ 0.36
	Br^{79}	50.51		–
	Br^{80}		18 min.	β^- 2.0; $\gamma \approx 0.5$
	$\odot Br^{80}$		4.5 hours	I; γ 0.049
	Br^{81}	49.49		
	Br^{82}		33.9 hours	β^- 0.465; γ 0.547-1.5
Tin	Sn^{121}		1.1 day	β^- 0.383
Iodine	I^{126}		13.1 days	β^- 0.85; γ 0.395
	I^{127}	100		–
	I^{128}		25 min.	β^- 1.59; 2.02; γ 0.428
	I^{131}		8 days	β^- 0.61; γ 0.08-0.64
Cerium	Ce^{144}		275 days	β^- 3.07; 0.85; γ 0.135
Mercury	Hg^{198}	10.12		–
	Hg^{199}	17.01		–
	Hg^{200}	23.21		–
	Hg^{201}	13.15		–
	Hg^{202}	29.66		–
	Hg^{203}			
	Hg^{204}	6.69	43.5 days	β^- 0.205; γ 0.272
Thallium	Tl^{204}		2.7 years	β^- 0.783
Thorium	Th^{230}		$8 \cdot 10^4$ years	α 4.62; 4.68
	Th^{232}		$1.389 \cdot 10^{10}$ years	α, Φ 3.90

TABLE OF CONTENTS

Page

Preface 3

Chapter I. Thermodynamical Isotope Effects 6

§1. Isotopes and Isotopic Molecules 6
§2. Concept and Examples of Isotopic Exchange 7
§3. Isotope Effects 10
§4. Isotope Effects in Chemical Equilibria 12
§5. Statistical Theory of Chemical Equilibria 14
§6. Statistical Sums for Translational and Rotational Energy 17
§7. Vibrational Statistical Sums 22
§8. Fundamental Equations for Isotopic Exchange Equilibrium 29
§9. The Bigeleisen-Mayer and Tatevsky Approximate Equations and Functions 35
§10. Isotopic Equilibria of Carbon 40
§11. Isotopic Equilibria of Other Elements (N, O, etc.) 45
§12. Isotope Effects in Adsorption 46
  a) Experimental data 46
  b) Theoretical evaluation 48
  c) Adsorption on heterogeneous surfaces 49
§13. Isotope Effects in Evaporation and Distillation 51
§14. Chemical Equilibria in Non-Ideal Heterogeneous Systems 53
§15. Relationship Between Enrichment Factors and Equilibrium Constants 55
§16. Isotope Effects in Hydrogen Equilibria 56
  a) The simplest reactions of hydrogen 56
  b) Molecular hydrogen 58
  c) Hydrogen compounds 67
§17. Distribution Coefficients of Hydrogen Isotopes Between Hydrides and Their Dependence on the Positions of the Elements in D. I. Mendeleev's Periodic Table 67
§18. Calculations of Isotope Effects with the Aid of Computer Techniques 70
§19. Experimental Verification of the Statistical Theory of Isotope Effects 72
  a) Gaseous reactions 73
  b) Exchange in heterogeneous systems 79
  c) Experimental data on the exchange of inorganic and organic substances in solution 81
§20. Summary 83
Literature Cited 83

Chapter II. Kinetics of Uncomplicated Isotopic Exchange 86

§1. Difficulties Encountered in Derivation of General Equations 86
§2. The Motive Force of Isotopic Exchange, True and False Equilibria 86
§3. Kinetic Types of Isotopic Exchange Reactions 90
  a) Early studies 90
  b) Types of isotopic exchange reactions 91
§4. Peculiarities of Isotopic Exchange Reactions Caused by Close Similarities in the Properties of the Exchanging Atoms or Groups 92

Page
§5. Simplo and Complex Isotopic Exchange Reactions. 99
a) Definition of simple and complex exchange 99
b) Homomolecular exchange system between two substances. 100
c) Exchange involving labile active forms 101
§6. The Exponential Variation of the Isotopic Concentrations of Molecules with Time. . . . 101
a) Initial concepts and designations. 102
b) Derivation of kinetic equations 103
c) Range of applicability of the derived equations 105
§7. Kinetics of Isotopic Exchange in Dynamic Conditions 105
a) Equations for the chemical dynamics of reactions proceeding without volume change 105
b) Dynamics of isotopic exchange 110
§8. Determination of True Kinetic Equations and Kinetic Constants for Isotopic Exchange. . 112
1. Significance of investigations of the dependence of the kinetic exchange constants on the initial and external conditions 112
2. Examples of isotopic exchange in the gas phase 113
a) Isotopic exchange of molecular hydrogen: $H_2 + D_2 \rightleftharpoons 2HD$. 113
b) Bromine and hydrogen exchange of gaseous ethyl bromide 115
3. Exchange in solutions. 117
a) Isotopic exchange of the chlorides of tin. 117
b) Isotopic exchange between Ce^{3+} and Ce^{4+} in acid solutions. 119
c) Isotopic exchange of iodide with iodate ions 121
d) Isotopic exchange of sulfur between disulfides and thiols in organic solvents. 121
4. Heterogeneous catalytic exchange. 124
Literature Cited. 125

Chapter III. Mechanisms and Stages of Isotopic Exchange. 128

§1. Exchange by Electron Transfer. 128
§2. Tunnel and Nonadiabatic Transfers 130
§3. Catalytic Action of Negative Ions on Isotopic Exchange of Cations. 136
§4. Isotopic Exchange Between Iron Ions 139
§5. The Reality of Direct Electron Transfers in Solutions. 139
§6. Isotopic Exchange Between Atoms and Simple Ions by a Dissociation Mechanism. 141
§7. Dissociative Heterogeneous Exchange. 147
§8. Association Mechanism. 147
§9. Associative Exchange with Formation of Intermediate Complexes Only 148
§10. Exchange with Transfer of Isotopes within Radicals, Molecules, and Polyatomic Ions. . 149
§11. Isotopic Exchange as the Result of an Elementary Chemical Reaction. 151
§12. Complete Stage Scheme of Isotopic Exchange 153
§13. Electronic Types of Isotopic Exchange Reactions. 155
§14. The Role of Tautomeric Regrouping in Isotopic Hydrogen Exchange. 158
§15. Characteristics of Hydrogen Exchange of Free Radicals and Its Role in the Exchange of Saturated Molecules. 162
§16. Ionic Mechanisms of Hydrogen Exchange in Hydrocarbons. 166
§17. The Electrophilic Nature of Hydrogen Exchange 179
§18. The Acid-Base Concept of the Hydrogen Exchange of Hydrocarbons. 182
§19. Contradictions in Views on the Mechanism of Deuterium Exchange, Their Origins, and Attempts to Remove Them. 187
§20. Mechanisms of Oxygen Exchange. 191
a) General characteristics of oxygen exchange. 191
b) Exchange of molecular oxygen by dissociation mechanisms. 192
c) Exchange of oxygen in water and anions. 195
§21. Isotopic Exchange of Halogens 197

Page
§22. Mechanism and Kinetics of the Exchange of Organic Halides. 200
§23. Mechanism of the Isotopic Exchange of Particles Forming the Internal Coordination Groups in Complexes 213
§24. Classification of Isotopic Exchange Reactions. 216
Literature Cited. 221

Chapter IV. Isotope Effects in Chemical Kinetics. 229

§1. Special Features of the Problem 229
§2. Statistical Theory of Isotope Kinetic Corrections 231
§3. Intramolecular Isotope Effects 235
§4. Experimental Data on the Magnitude of Intramolecular Kinetic Isotope Effects 240
§5. Kinetic Effects in Reactions of Other Types in Solutions. 240
§6. Isotope Effects in the Kinetics of Hydrogen Reactions. 244
§7. Maximum Theoretically Possible Values of Kinetic Isotope Effects. 245
§8. Effect of Substituents on the Activation Energies and Entropies of Reactions 246
§9. Hidden Thermodynamic Isotope Effects in Kinetics. 249
§10. Isotope Effects in the Kinetics of Catalytic Reactions. 251
§11. Kinetic Isotope Effects in Contact Reactions of Hydrogen 255
a) Decomposition of ammonia. 255
b) Oxidation of hydrogen 256
c) Other gaseous catalytic reactions 257
§12. Kinetic Isotope Effects of Processes Related to Heterogeneous Catalysis 259
a) Adsorption. 259
b) Desorption. 260
c) Diffusion of hydrogen through metals. 262
d) Topochemical reactions 262
§13. Comparative Action of Hydrogen Isotopes in Acid-Base Catalysis 266
a) Halogenation of ketones 272
b) Nitration of aromatic compounds 275
§14. Kinetic Isotope Effects in Homogeneous Gaseous Reactions 278
a) Simple reactions of atoms and radicals 279
b) Isotope effects in unbranched chain processes. 282
c) Branched chain processes. 285
d) Nonchain reactions with a molecular mechanism 288
§15. New Trends in Investigations of Hydrogen Isotope Effects 291
§16. The Significance of Isotope Effects in Chemical Kinetics 294
Literature Cited. 294

Chapter V. Kinetics of Complicated Isotopic Exchange 302

§1. Main Types of Complications. 302
§2. Complications of Isotopic Exchange Kinetics Caused by the Participation of More than Two Forms 302
§3. Transfer and Conjugation in Isotopic Exchange. 305
§4. Conjugation Involving Tautomeric Regrouping. 306
§5. The Kinetic Additivity of Complicated Isotopic Exchange 310
§6. Kinetics in Presence of Two Independent Acceptors. 316
§7. Statistical Theory of Exchange in a System with a Large Number of Acceptors 328
§8. Complications of Isotopic Exchange Kinetics Caused by Thermodynamic Isotope Effects 334
a) Approximate equations for molecules containing several atoms of the exchanging isotope in the same chemical position 334
b) Allowance for nonideality of the exchange 335
§9. Determination of Isotopic Corrections from the Separation Kinetics 337
§10. Kinetics of Isotopic Exchange with Superposition of Processes of Different Types 342
Literature Cited. 345

Page

Chapter VI. Main Fields of Application and Development Prospects of Isotope Methods in Chemical Kinetics 348

- § 1. Leading Problems in Chemical Kinetics 348
- § 2. Isotope Methods for Studying Ordinary (Elementary) Chemical Reactions 351
  - a) Complex character and steps in chemical reactions 351
  - b) Tests for the equivalence of different atoms 352
  - c) Determination of the kinetic roles of different atoms of a particular element in a process 354
- § 3. The True Genetic Relationships of Stable Molecules Which Participate and Appear in Complex Reactions 356
  - a) Oxidation reactions 356
  - b) Determination of genetic relationships and verification of the mechanisms in other types of reactions 361
- § 4. M. B. Neiman's Kinetic Isotope Method 363
- § 5. Detection of Intermediate Labile Forms and Verification of Chain Mechanisms 366
  - a) The significance of labile forms 366
  - b) Methods based on deuterium exchange 366
  - c) Tagged atoms and radicals 369
- § 6. Determination of the Structure of Intermediate Complexes and of the Nature of the Bonds Broken and Formed at the Rate-Determining Stage 370
- § 7. Isotopes in Catalysis 372
  - a) General kinetic and specific problems of catalysis 372
  - b) The manner of catalyst participation in a catalytic process 372
  - c) Chain reactions in catalysis 375
  - d) Active forms of heterogeneous catalysis 377
- § 8. Isotope Methods for Investigation of Catalysts 379
- § 9. Isotope Methods for Investigation of Surface Inhomogeneity and Interaction Between the Adsorbed Molecules 384
  - a) Inhomogeneity and repulsion 384
  - b) The differential isotopic method 385
- § 10. Potentialities of the Use of Isotopes for Studying the Reactivity of Matter 387

Literature Cited 389

Appendix 397
- I. Tables of Thermodynamic Functions 397
- II. Tables of Isotopic Exchange Equilibrium Constants 433
- III. Tables of Kinetic Isotope Effects and of Isotopic Exchange Kinetics 442

Conventional Signs 447

Index of Isotopes Mentioned in the Text; and Their Properties 450

STAT