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The Chemical Separation of the Elements
and Isotopes Formed During Fission of Uranium
(General Part)

Otto Hahn and Fritz Strassmann

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ISOTOPES
THE CHEMICAL SEPARATION OF THE ELEMENTS AND ATOM VARIATIONS FORMED
FISSION
DURING THE SPLITTING OF URANIUM

(GENERAL PART)

OTTO HAHN AND FRITZ STRASSMANN

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FOREWORD

In a report, "Notes Concerning the Experimental Unraveling of the Elements and Atom Variations which Occur During the Splitting of Uranium", (O. Hahn, F. Strassmann and H. G^otte, Trans. Preus. Acad. Sciences, 1942, Math. - Science Series Number 3.) it was shown by a number of examples how conclusions could be drawn from the activity curves of the products as to the uniformity or multiplicity of the atom variations involved. It was also shown whether isotopes of the same elements or transformation series were involved. The method of unraveling was systematically presented by using the example of the numerous strontium isotopes -- their transformation products and their mother substances, -- which occur during splitting. The significance was pointed out which the changes of the physical working and measuring conditions for the interpretation of the processes involved.

Methods for the chemically pure production of the elements were only occasionally referred to.

A number of active isotopes, well suited for indicator experiments, are present among the fission products, and these isotopes are of significance. A number of these active isotopes cannot be produced or have until now not been produced according to nuclear processes. Other^S_A are prepared from uranium rather than by the usual methods from the same or neighboring elements. This presents considerable advantages. Therefore it is desirable to describe the chemical separation of the fission products and to examine in detail methods of producing short-lived isotopes. Of special interest are the short-lived substances, for they are the suspected initial units of the transformation series. For this

reason methods used here differ in several respects from the known, proved analytical separation methods due to the necessity of rapid procedure. Before treating the actual topic something should be mentioned concerning the operation with radioactive atom variations. Essentially these are observations collected over a period of years at the Kaiser-Wilhelm Institute for Chemistry. General information concerning the processing of uranium, the separation of the rare gases, reference to the method of analysis with several analytical short cuts, and information concerning the processing and measurement of the products is given. Systematic description of the separation of individual elements and their isotopes will follow later in a second part.

DIFFERENCE BETWEEN CHEMICAL AND RADIOACTIVE METHODS

An essential difference exists between chemical and radioactive methods of investigation. In the case of the usual chemical reactions the unchanging, stable elements are investigated. To do this trillions of atoms or molecules are generally necessary. In the case of radioactive methods the atoms which transform themselves during the measurement are measured by radiation particles which are thereby emitted. Thus the atoms which transmute in a given length of time, not the number of those present, are a standard of proof. Accordingly the analysis of chemical elements is superior to analysis of normal chemical reactions. It is possible to trace the emitted radiation particles to the individual atoms which emit the particles. This is made possible by the great amount of energy with which the radiation particles are emitted from the transmuting atoms. The resulting strong ionization of the gas molecules struck by the particles is sufficient for the analysis of the individual radiation particle in a Wilson cloud chamber or a counter.

THE SMALLEST AMOUNTS OF SUBSTANCE RETAIN THEIR SPECIFIC PROPERTIES

Since the analysis is so sensitive, we ask ourselves, to what degree do the atoms of the elements retain their specific chemical properties? Do the characteristic reactions eventually stop? It may prove interesting to review the investigations by Strassmann and Hahn which led to the discovery of the splitting of uranium.

We found several synthetically-active atom variations during the exposure to radiation of uranium with neutrons which we thought to be radium isotopes. A few thousand atoms were involved with weight quantities of approximately one trillionth of a gram. Barium, being very similar to radium, served as the carrier agent for these minute quantities. The presumed radium isotopes did not behave quite as we had assumed for radium. We were unable to separate it from barium by fractional distillation despite the fact that we used methods which had proved themselves through many years of experience in the separation of radium or its isotopes, mesothorium and thorium X from barium. We prepared minute active quantities of natural radium isotopes, mesothorium and thorium X, to prove whether the few thousand atoms of our synthetically-active atom variations behaved other than as known chemically-characterized element representatives. The minute quantities behaved exactly as supposed. They concentrated as chlorides and bromides and diluted as carbonates. We then mixed the weak synthetic isotopes with the weak natural isotopes. Repeating the fractional distillations with barium, we observed that the natural radium eventually separated from barium as supposed. However, the synthetic radium did not. This proved the fission of

uranium. These experiments show that the chemical properties are retained down to the most minimal of concentrations.

APPARENT EXCEPTIONS IN THE CASE OF SURFACE-RICH PRECIPITATES

During the work with active atom variations, exceptions contrary to the chemical nature of their elements appear at times. In that case the inactive element will behave under the given conditions just like the much more easily analyzed active element. Apparent exceptions of this nature are frequently encountered.

It is known that lead salts do not precipitate with an excess of sodium hydroxide, but do so with ammonia. If, for example, small quantities of ferric salts which contain the lead isotope ^{210}Pb are precipitated with excess sodium hydroxide the lead does not remain in solution. It precipitates quantitatively exactly with ferric hydroxide as in the precipitation with ammonia. The small quantities of lead are adsorbed by the ferric hydroxide precipitate. Ordinary lead reacts in the same manner. The adsorption may be demonstrated by gradual addition of inactive lead to active lead.

A method of separating uranium from uranium X depends upon a similar process. Uranium is precipitated together with ferric hydroxide as ammonium uranate with ammonia, and the ammonium uranate is brought into solution again by treatment with ammonium carbonate. One would expect, that the thorium isotope uranium X, precipitated with iron, would again go into solution, since thorium hydroxide is soluble in ammonium carbonate. But it remains adsorbed to the iron precipitate despite the fact that weighable quantities of thorium hydroxide could be separated from iron in this manner.

On the other hand, unweighable quantities of a uranium isotope could be separated from weighable quantities of thorium in the same manner. The uranium would be adsorbed by the ferric hydroxide, and the thorium would go into solution.

In the case of surface-rich, amorphous, or microcrystalline precipitates, atom variations, which do not belong to the precipitates, may be carried over. The precipitate must therefore be dissolved and reprecipitated in order to be purified. This is done by adding, in weighable quantities during the dissolving and reprecipitation, the foreign element which contaminates the precipitate. This added element strongly dilutes the active isotope atom variation which is to be separated. The newly adsorbed component is radioactively no longer or hardly detectable. Subsequent dissolving and reprecipitation under the same requirements will complete the separation of resistant atom variations which were carried over. The quantity of the inactive element to be added depends upon whether the active atom variation, introduced with the added element and to be separated from the surface-rich precipitate, is to be obtained or not. If active atom variations are to be separated in small weighable quantities, then too large additions to the added inactive atom variations may interfere.

The group separation of "rare earths" from the alkali earth metals is an example from the "uranium fission". The earths are precipitated with ammonia, free from carbon dioxide, using several milligrams of iron as carrier. To prevent the simultaneous precipitation of active barium and strontium, 100 to 200 milligrams of barium or strontium or both elements are added. After repeated dissolving and reprecipitation the iron is absolutely free from the

active alkali earth metals, even though the ammonia was not completely free from carbon dioxide. The earths which were precipitated with the iron may now be separated without fearing that yttrium and lanthanum isotopes will reform from the remains of the not too remote strontium or barium, the mother substances of the yttrium and lanthanum.

ADVANTAGES OF COARSELY CRYSTALLIZED PRECIPITATES

Surface-weak, crystallized precipitates have a weak adsorption ability for foreign atom variations. This enables one to frequently separate the radio-active isotope from the salt of the inactive isotope carrier-element in a mixture of various active atom variations by a single precipitation. Good examples of this are found during the processing of numerous isotope-mixtures which occur during the splitting of uranium. It is possible, for example, to obtain in a practically pure state the synthetically active barium isotopes after adding weighable barium quantities. This is obtained from a hydrochloric acid solution of the ^{ir}radiated uranium by means of concentrated hydrochloric acid after a single precipitation of barium chloride. This is true even in the case of reprecipitation of the barium, where it is obtained absolutely free from all other dissociation products, uranium, and its transformation product U X. The barium yield is however not entirely quantitative. However, the yield may easily be determined in the usual manner by a barium determination. If barium sulfate, which is usually used for quantitative barium precipitation, were chosen instead of the barium chloride, which is difficultly soluble in strong hydrochloric acid, the surface-rich barium sulfate would be partly adsorbed together with a number of other synthetically active

atom variations including uranium and uranium X. This method, therefore, would not achieve the purpose.

Equally favorable methods of separation are available for cesium in cesium silico tungstate, uranium in uranyl-sodium acetate, zircon in zircon oxychloride. In the latter case, however, active barium may not be present with weighable quantities of barium. In the strong hydrochloric acid solution from which the oxychloride is precipitated the barium would also be precipitated as chloride. Active zircon as well as active barium would be present in the precipitation mixture.

Good crystallization ability of the precipitates is a prerequisite for reactions yielding only pure isotopes. It is not even necessary that the active atom variation which is to be precipitated be an isotope with the inactive binding constituent. It is sufficient that the active atom variation forms mixed crystals with the binding constituent in the separation used for precipitation. Thus barium is precipitated with Sr in strontium nitrate, Cs with Rb-stannic chloride, and element 93, valence 6, with the uranyl sodium acetate.

PREPARING THE URANIUM, WHICH WAS EXPOSED TO RADIATION, FOR ANALYSIS

Artificial radiation sources used in Germany and the use of radium-beryllium products as neutron sources, make it necessary to completely separate the uranium in order to obtain individual fission products. The β -radiation uranium X, which originates from uranium makes this necessary. Ten grams of uranium show a β -activity of more than 1 million particles per minute in a Geiger-Müller counter as a result of uranium X. The yield of the

individual fission products is at least three magnitudes smaller when using one gram radium + beryllium as a neutron source, even when the slowed neutrons are active in a favorable position of the product. In order not to obtain the fission products in a too low intensity, greater quantities of uranium (up to several hundred grams) must be exposed to radiation.

Various alternatives for processing the uranium present themselves, according to the quantity of uranium exposed to radiation. If several 100 gram quantities of uranium were exposed to radiation, the uranium will be present in the form of a nitrate. Consequently it is insignificant whether the exposure to radiation of the uranium takes place in solution or in the form of solid salt. If the uranium nitrate is crystallized by fractionating it several times, the first crystal fractions of the uranyl nitrate contain practically no fission products. The greater part of the uranium may be removed in this manner. However, the total quantity of the uranium X remains in the lyes with the fission products and must be separated from them later. Subsequent processing may proceed in various manners, depending upon which fission products are preferred. (Special Part).

The "ether-method" is used to obtain smaller quantities of uranium more rapidly. The uranium is exposed to radiation as crystallized, hydrous nitrate, and after the exposure to radiation it is dissolved in ether in a separatory funnel. For each 10 grams of uranium salt 10 cubic centimeters of ether are necessary. The watery phase obtained from the crystal water contains small quantities of uranyl nitrate and practically all fission products. By repeated extraction of the ether solution with a small quantity of

water, the fission product yield can be improved. This also increases the uranium quantity, which must again be separated later. This method permits the separation of approximately 90 percent uranium from the fission products, using limited quantities of uranium, and within only a few minutes. Uranium X is still present in the fission products. Three methods are available for further processing:

(1) The separation of uranium as sodium pyrouanate by precipitating the uranium solution with sodium hydroxide. The separation of the largest part of the synthetic alkali and alkali earth metals from uranium and uranium X results.

(2) The dissolving of uranium into uranium ammonium carbonate, by dissolving the precipitate in excess ammonium carbonate. The uranium was precipitated as ammonium pyrouanate with ammonia. Separation of uranium from synthetically active earths, zircon, niobium, etc, results. Uranium X remains among the earths.

(3) The precipitation of uranium as uranyl sodium acetate by precipitation with sodium acetate from an acetic acid solution. The separation of the largest part of the uranium from all fission products including uranium X results.

Further details are discussed in the special part.

A prior separation of uranium is not necessary for the production of a series of fission products, as in the case of metals precipitated with H_2S . The alkali earths, barium and strontium, may also be directly obtained from the uranium product which was exposed to radiation. Uranium in the form of ammonium pyrouanate is selected for the purpose of exposure to radiation. This is

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easily obtained by precipitating a uranium salt with ammonia. The precipitation of barium results from the uranate dissolved in concentrated hydrochloric acid. To separate the strontium (plus barium) the uranyl nitrate is used since this precipitation occurs from a concentrated, nitric solution. (Details to follow later). These alkali earth metals are easily separated in pure form. This facilitates the preparation of the metabolons, lanthanum, cerium, and yttrium.

SEPARATION OF THE RARE GASES FROM URANIUM

The spatial elimination of the rare gases xenon and krypton which form during the uranium fission present an excellent method for the production of a whole ~~series~~ ^{series} of fission products. These two gases are separated from the uranium during or after exposure to radiation by means of a stream of air which is conducted through the uranium solution. They may be measured directly or be separated at low temperatures from the adsorption agents, in which case they will form the decay products. A complete separation of krypton from xenon, and consequently rubidium, strontium, and yttrium from cesium, barium, and lanthanum is achieved by regulating the temperature selected for adsorption. Transformation products of a short half-life period cannot be obtained by the latter method, because the processing of the adsorption agent requires several minutes.

A method exists for obtaining transformation products of the rare gases which have a short life. This process resulted from experience with the so-called "emanating-method" used at the Kaiser Wilhelm Institute for Chemistry. A uranium product is produced in such a surface-rich form that it is marked by a high

emanating ability while in a dry state. The rare gases, originating during exposure to radiation, diffuse in high percentage quantities from the surface-rich salt. Their transformation products are separated as invisible "active precipitates" on a negatively charged metal plate or foil and may be removed by acid within a few seconds. This method yielded cesium of 110 seconds half-life, and a rubidium of 80 seconds.

A detailed discussion of the separation of rare gases and their transformation products by spatial separation of the gases from uranium will not be entered into here.

The separation of fission products which are easily distilled off in elementary forms or as chemical compounds is similar in certain respects. This includes iodine, bromine, and certain platinum metals.

A DIFFERENT ANALYSIS FOR SHORT-LIFE OR LONG-LIFE ISOTOPES

It has already been pointed out that in the case of larger quantities of uranium exposed to radiation, the main quantity of uranium is removed first of all prior to the actual separation of the individual fission products, in order to obtain smaller processing volumes. The quantities of uranium to be used for radiation depend upon the experimental purpose in addition to the available radiating source. For the mere purpose of proving individual active fission products, smaller uranium quantities are needed than for obtaining already known isotopes of greater intensity, which may be used for indicator experiments. In order to determine the chemical nature and the radioactive constants of one or several active atom variations after exposure to radiation, the presumed

elements to which the synthetic atom variations presumably belong are added in weighable quantities. If not too short-lived substances are involved, the usual separation procedure of analytical chemistry is applied.

Proved analytical precipitation methods can only rarely be used in the search and separation of short-life fission products. When the available radiation sources are not too extremely strong, then the separation must take place so that not more than four to five half-life periods of the substance to be obtained have passed between the end of the radiation and the beginning of measurement. After this time only 6-3 percent of the originally available intensity is left as initiating activity. The method of separation is determined by the requirements of speedy separation, specific precipitation of the element concerned, and the insolubility of the precipitate under precipitation requirements. A truly quantitative separation in the sense of the analysis cannot be quite attained under these circumstances. Sufficient practice enabled measurement of substances with half-life values of $\frac{1}{2}$ -1 minute and radioactively pure, $1\frac{1}{2}$ -2 minutes after interruption of exposure to radiation. Neutron source, laboratory, and measuring room should be close together to conserve time.

It is necessary to know which fraction of the fission products were obtained during the rapid separation operations, if yield determinations for the individual fission processes are to be carried out. This is not difficult after the decomposition of the isotopes concerned. The quantity of the element pertaining to the active isotope, added before the analytical separation, must be known. The yield of the element concerned is determined after

the measurement, using proved methods of analysis. The subsequent yield determination by precipitation of the measured preparation, as with barium sulfate, results if the barium was precipitated and measured as chloride from an added, known quantity of barium added to uranium which had been exposed to radiation. Purely analogous methods are used with the other elements.

SEVERAL ANALYTICAL SHORT CUTS

It was previously pointed out that the element with its active isotopes are not present alone in the precipitate during the separation of well-crystallized precipitates. There also are isotopes of such elements which form mixed crystals with the precipitated element. If larger quantities of strontium are precipitated as nitrate, the unweighable quantities of active barium isotopes which may be present are also precipitated as mixed crystals. The active barium is separated from the strontium as chromate by minimal quantities of weighable barium after the purification of the strontium precipitate. This indirect method of barium separation is recommended if the active barium is to be obtained in a highly concentrated form. Too many of the desired active isotopes are retained in solution during the simpler, direct separation of barium as chloride. This is due to the solubility of the chloride, which is not to be neglected, in concentrated hydrochloric acid, even though only small quantities of barium are used.

Strontium is obtained in highly concentrated form by precipitating the nitrate with barium as a carrier and carrying out the barium-strontium separation after adding very small quantities of strontium.

Another example of the use of a mixed crystal formation is the concentrating of element 93 with the chemically similar uranium. The element 93 together with uranium as uranyl sodium acetate is precipitated in a mixed crystal-like form in an oxidized (valence 6) state. In this manner it is liberated from the uranium fission products. Element 93, with a valence of 4, to which it easily changes, does not form any mixed crystals with the uranyl salt, and may be easily separated from the uranium in this manner.

One is not limited to only coarsely crystalline precipitates, even though these rapidly yield pure preparations. It is not advisable to separate thorium from the earths by addition of weighable thorium quantities because of their natural activity, when the β -radiating thorium isotope uranium X is separated from the earths originating during the fission of uranium. Therefore zircon is selected as carrier for uranium X. If it is desired to separate active zircon isotopes from uranium X after the separation of the earths, a reaction is selected in which thorium and zircon differ. An inactive earth may be selected as carrier for thorium.

It is not difficult to find a method for separating an element to be separated in a small quantity of weight. This is achieved by using a chemically similar inactive element in larger quantities, which behaves differently. This permits the separation of the element from all other non-desirable elements. To obtain the active element, in light-weight quantities, it is necessary to separate the added inactive carrier.

Among the numerous fission products of uranium, some elements are obtained radioactively pure much more easily than others. The separation of the rare earths from one another and from uranium X

requires experience and takes considerable time because of the presence of active contaminations in the form of strongly adsorbed precipitates. It is fortunate that the earths are decomposition products of the alkali earth metals which are easily obtained in a pure state in coarsely crystalline form. The daughter substance may be simply obtained from the mother substance rather than from the complicated mixture of numerous fission products when the mother substances do not have too short a half-life period in comparison to their transformation products. Important yttrium and lanthanum isotopes may be separated from the strontium and barium isotopes in this manner. Similarly niobium may be separated from zircon, praseodymium from cerium, iodine from tellurium as well as some platinum metals. If the half life of the mother substance is much greater than that of the daughter substance, the latter is always easily separated again. The previously-mentioned separation of the rare gases from the uranium solution or from the "highly emanating" uranium salt makes use of the same advantage of easy separation from mother substances.

PROCESSING AND MEASUREMENT OF THE PRECIPITATES

The separation and purification of the numerous precipitations, which arise during the processing of the uranium exposed to radiation, require numerous filtrations, which often must take place very rapidly. The usual funnels and doubly-folded filters were not used. Simple, porcelain funnels, consisting of two parts, proved very useful. Illustration I shows such a funnel assembled on the filter support and disassembled on the left hand side of the illustration.

ILLUSTRATION I [see page 18]

The two parts are abraded with respect to each other. Hardened filters from Schleicher and Schüll were used. In most cases however, membrane filters from the Membrane-Filter-Society of Göttingen were used. A funnel with a diameter of 4 centimeters is used for the separation of active isotopes with an added carrier element. Funnels, 7 centimeters in diameter, are used for larger precipitation quantities. The funnels may be obtained from the Federal Manufacturer of Porcelain in Berlin. Similar glass funnels may be obtained from Schott and Company.

Since all precipitates are removed by suction, no liquid escapes from the sides of the funnel parts.

The filtration and washing are rapid. The upper part of the funnel is removed toward the end of the washing and the edge of the filter is washed. After drying (not over 150 degrees if membrane filters are used) the smooth filtrate is directly available for measurement in the counter. Before measurement the filtrate is covered with a foil of very thin adhesive cellophane, which was provided by Kalle and Company Biebrich a. Rh. in strips of proper width.

The measurement of activity follows in the general fashion in a Geiger-Müller counter. To shield a part of the penetrating radiation (γ -rays and cosmic rays in the air) the counter is enclosed in a thick lead casing, as shown in the illustration. A standard measurement is regularly made with a thin layer of uranium oxide or a piece of uranium glass for comparisons of activity and for measurements repeated over an extended time span. The obtained activities are converted to the same standard.

If sufficient counters are available, it is recommended that a thin-walled (5 or 10 μ) counter is available for the detection of easily absorbed β -rays in addition to the usual 100 μ -counter. A conclusion concerning the purity of the preparation in question may be drawn from the "softness" of a certain radiation. The use of the same counters for disintegration measurements, occurring over periods of months or years, is discouraged. Counters used for frequent control measurements of precipitates which are still to be processed are overburdened and frequently become defective.

The evaluation of the activity curves for the disentanglement of the isotope mixtures and their transformation series was dealt with in the report (Pruss. Acad. Sciences) mentioned in the foreword.

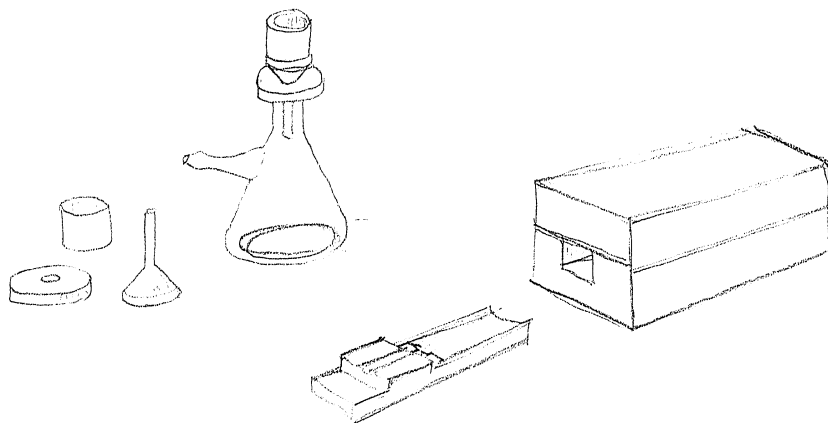


Figure 1.

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