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DETERMINATION OF THE RATE CONSTANT FOR THERMAL
CRACKING OF METHANE BY ADIABATIC COMPRESSION
AND EXPANSION

STAT

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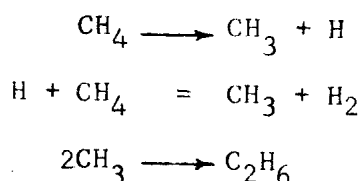
The method of adiabatic compression and expansion worked out by Ryabinin^{1/} more than ten years ago has not found due application in measuring rate constants of elementary chemical reactions at high temperatures and pressures. The possibility of such an application was shown only recently by Markevich et al.^{2/} for the thermal cracking of methane. It was ascertained that due to specific temperature variations in the course of compression and expansion, calculation may be made considerably less tedious.

The experimental data obtained in this work permit fairly accurate determination of the rate constant for unimolecular decomposition of methane molecules. The following conditions may be considered as most favorable.

1. With a system containing a low percentage of the reacting gas considerably diluted with some inert gas, for example argon, the reaction-induced variations in temperature may be neglected and the reaction considered as strictly adiabatic.

2. Since under adiabatic compression the reaction becomes measurable only at temperatures and pressures higher than certain limiting T^* and p^* values which differ only slightly from T_{\max} and p_{\max} , $\delta = \frac{C_p}{C_v}$ may be considered as constant throughout the ranges of $T_{\max} - T^*$ and $p_{\max} - p^*$.

3. Hydrogen and ethane were shown to be the main reaction products of the initial reaction (i.e., at low compression)^{2b/}. Consequently, under these conditions the reaction will follow a simple mechanism.



Under the assumption of a stationary H atom concentration, the rate of hydrogen formation will be

$$\frac{d(\text{H}_2)}{dt} = A_1(\text{CH}_4)e^{-E/RT}$$

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where A_1 is the frequency factor in the rate constant for the reaction $\text{CH}_4 = \text{CH}_3 + \text{H}$. The data obtained by Markevich et al., ^{2b/}, as well as the majority of other published data, seem to be in favor of a unimolecular mechanism for this reaction (under the experimental conditions used).

4. Due to the high activation energy E , the reaction proceeds at a temperature close to T_{max} . This assumption is similar to that taken as a basis for the theory of thermal flame propagation by Zeldovich and Frank-Kamenetzki^{3/}, namely, that combustion proceeds at a temperature differing only slightly from the maximum combustion temperature.

Introducing the value $\gamma = \frac{(\text{H}_2)}{(\text{CH}_4)}$ and making use of the first three conditions, we obtain, after certain transformations, on the basis of the assumed reaction mechanism and from the equation for piston motion,

$$d(\gamma \alpha) = -x_0 \frac{A_1 e^{-E/RT} dT}{T \sqrt{\frac{2(\gamma-1)}{m} \frac{p_0 V_0}{T_0} (T_{\text{max}} - T)}}$$

where x_0 is the length of the reactor channel, m is the piston mass, and p_0, V_0, T_0 are the initial pressure, volume and temperature.

Integration, making allowance for the fourth of the above conditions, gives

$$\gamma^* \alpha^* = x_0 \frac{A_1 e^{-E/RT_{\text{max}}}}{\sqrt{\frac{E(\gamma^*-1)}{2m} \frac{p_0 V_0}{RT_0}}} \chi^*$$

where γ^* is the final value of the $(\text{H}_2)/(\text{CH}_4)$ ratio, α^* is the degree of compression at $T = T^*$ and

$$\chi^* = \frac{2}{\sqrt{\pi}} \int_0^{\xi^*} e^{-\xi^2} d\xi, \quad \xi^* = \sqrt{\frac{E}{RT_{\text{max}}} \left(1 - \frac{T^*}{T_{\text{max}}}\right)}$$

It will be seen from the last expression that by plotting $\lg \frac{\gamma^* \sqrt{\gamma^*-1}}{\alpha^*}$ versus $\frac{1}{T_{\text{max}}}$ we obtain a straight line, and that the E and A_1 values

may be derived from its parameters. A straight line of this kind plotted from the data of ^{2b/} would yield the following rate constant for unimolecular decomposition of methane molecules:

$$k_1 = 1 \times 10^{15} e^{-103000/RT} \text{sec}^{-1}$$

Of all the rate constants for the decomposition of methane molecules, the most accurate seems to be that determined by Skipper and Ruherwein^{4/}

$$k_1 = 10^{14.71} e^{-101000/RT} \text{sec}^{-1}$$

which, in fact, coincides with ours.

Let us add that, according to Nikitin, at temperatures considerably lower than the characteristic temperature for the slowest vibrations of the CH₄ molecule (1860°K), the rate constant for bimolecular decomposition of methane CH₄ + Ar = CH₃ + H + Ar is $k_2 = 10^{21} e^{-E/RT} \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$, with an accuracy to within a power of ten. From general considerations based on the theory of unimolecular reactions, a reaction will be first order when the rate of activation, i. e., the rate of a bimolecular step, is considerably higher than that of an active molecule decomposition. The pertinent condition of unimolecularity is expressed by the inequality

$$A_2(\text{Ar}) \gg A_1$$

where A_2 is the frequency factor in the rate constant of a bimolecular reaction. The validity of this inequality will be apparent if we assume that $A_1 = 10^{15} \text{sec}^{-1}$, $A_2 = 10^{21} \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$ (see above) and $(\text{Ar}) = (\text{Ar})_0 \alpha = 2.5 \times 10^{19} \times 20 : 6 \times 10^{23} = 10^{-3} \text{mole cm}^3$. This may be considered as evidence that the thermal dissociation of methane under experimental conditions^{2b/} obeys a strictly unimolecular law.

For the determination of rate constants of elementary chemical reactions, the method of adiabatic compression and expansion seems no less accurate than the shock tube method.

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ON THE NATURE OF THE CRITICAL DIAMETER

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It has been established by many investigators concerned with the detonation of liquid explosives that the shock front of a detonation wave is not smooth. As in gas detonations, oblique shocks due to instability of the ignition plane travel over the detonation wave front. The ignition plane instability is a function of the temperature dependence of the reaction.

In traveling over the shock front of a detonation wave, the oblique waves collide and initiate a reaction. The induction period of the latter at the points of collision is considerably shorter than that observed beyond the shock front.

Consequently, initiating centers will not form when the conditions for intercollisions and collisions with reactor walls are unfavorable. When detonation passes from the tube into the air, the oblique waves at the edge find nothing to collide with. Thus no active centers will form at the shock periphery at the point of detonation exit. As a result, there will be no formation of new oblique shocks at the periphery of the detonation near the exit, and this, in turn, will lead to the disappearance of neighboring initiating centers. This may be seen from smear-camera records obtained for the detonation of transparent explosives, as observed from the butt end.

It was shown experimentally that detonation will proceed at the same rate if reaction-quenching waves do not penetrate as far as the axis of the charge. When they reach the latter, detonation stops. It will be apparent from this that the reaction-quenching waves may penetrate to a distance equal to one-half the critical diameter.

Let us consider what governs the penetration of reaction-quenching waves. After destruction of the oblique shocks, there remains a smooth shock wave at the detonation periphery; it is compressed by detonation products, as by a piston. The main shock compresses the explosive and initiates a reaction after a certain induction period τ which depends upon the temperature and pressure behind the wave. A rarefied wave comes from the charge edge at a rate C , thus the reaction has to occur at a place unattained by this wave, after a time τ . The reaction will then proceed into the charge as a detonation over the shock-compressed substance. It overtakes the reaction-quenching wave at a distance d_{cr} and stops the destruction of oblique waves.

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An equation for the critical diameter of detonation of a liquid explosive may be obtained on the basis of the above considerations.

$$d_{cr} = 2 \sqrt{U} \left(\frac{1}{D - U} + \frac{1}{U - C} \right) \quad (1)$$

Here V is the velocity of oblique shocks traveling over the detonation front; U is the velocity of the explosive compressed by the shock relative to the boundary of the quenching wave; D is the rate of detonation propagation over the compressed substance.

It follows from the above equation that, besides depending on kinetic parameters of the explosives, d_{cr} is a function of the mechanical properties of the explosive and its detonation products. It is also quite conceivable that a more active substance would have a higher d_{cr} , due to its mechanical properties.

Equation (1) was used to calculate d_{cr} for nitromethane (NM) at 1° to 20°C and for melted trotyl (TNT) at 82° to 83°C. The value obtained for NM was $d_{cr} = 14.3$ mm, as compared to the experimental 18 mm; for TNT the calculated value was 62, and the experimental was 68 mm.

CHARACTERISTICS OF LAMINAR AND TURBULENT FLASHBACK

STAT

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The laminar flame flashback mechanism seems to be clear if one considers a combustible gas mixture issuing from the port of a cylindrical tube. The Lewis and von Elbe "gradient flame flashback theory" has now received conclusive proof based on numerous experimental data for the burning of many gaseous but unheated mixtures.

Fewer investigations, however, have been dedicated to flashback under other conditions: at high laminar burning velocities, particularly in preheated mixtures, or when the gas velocity profile differs from the classical type for laminar steady flow in tubes (parabolic profile). The fundamentals of the flashback in turbulent flow also need further clarification. In this field, experimental data are limited and no attempts have been made to establish criteria for their evaluation.

This paper describes and discusses the influence of some factors which are essential from the standpoint of the flame flashback, such as the wide variation of the laminar burning velocity, the type of gas velocity profile of the stream issuing from the burner port (tubes, nozzles), the burner diameter variation, the state of flow (laminar or turbulent), and the type of mixture.

Experimental Results

Laminar flashback in tubes. The influence of pre-heating methane-oxygen mixtures on the flashback velocities was investigated at temperatures ranging from 20° to 400°C., for a wide range of mixture compositions. Such investigations were made also with regard to the laminar (normal) burning velocity. It was noted that the velocity gradient, g , increased considerably with increasing temperature but somewhat more slowly than the laminar burning velocity, U_b , and not as would have been expected from the results for unheated mixtures, where it was proportional to U_b^2 . This is explained by the nature of the heat conductivity coefficient, a , which is practically independent of the mixture composition but rises markedly with the temperature.

Taking into account the temperature dependence of a and using the experimental data for the flashback velocity w and for U_b , one can obtain good agreement with the well-known Putnam and Jensen relation,

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$$Pe = kS^2 \quad (1)$$

where $Pe = \frac{wd}{a}$ and $S = \frac{U_b d}{a}$

The coefficient k was found to be 0.01 which is close to the corresponding value of Putnam and Jense, $k = 0.0125$.

It should be noted here that the maximum value of U_b reached in the experiments under discussion was $U_b \sim 1500$ cm/sec., which is 30 times higher than that obtained hitherto when investigating flashback phenomena.

Laminar flashback in nozzles. Here, methane-air mixtures and nozzles of different shapes and sizes were used. It was found that the flashback depended upon the ratio of the inlet nozzle diameter to the outlet nozzle ($D:d$); if this ratio increases, the flashback velocity increases too, even when the outlet diameter is smaller. Correspondingly, the greater difference between these diameters, the higher the flashback velocity, so that the latter may sometimes reach the blowout velocity. This is due to the great uniformity of the velocity profile at the nozzle port, which is characterized by a sharp drop in velocity at the center of the stream. Special washers of different thickness were used to vary the velocity distribution at the nozzle orifice. Thus, different flashback velocities could be achieved. Two typical regimes were observed; with a short nozzle the flame had a meniscus shape and flashed back along the nozzle axis; when on the contrary the nozzle was long, the flame had the usual Bunsen cone form and flashed back near the tube wall.

Correspondingly, in these two regimes one may observe different relations between the flashback velocity and the length of the nozzle orifice, h ; for a short nozzle w diminished with increasing h ; for a long nozzle the result was quite the reverse. When the velocity profile was plane, the flashback velocity reached minimum and equaled U_b . Thus, quite different results may be obtained depending upon the actual radial velocity profile of a nozzle orifice.

Turbulent flashback. Turbulent flame flashback in methane-oxygen, methane-air and hydrogen-air mixtures was investigated using cylindrical tubes of different diameters. It was found that contrary to laminar flashback, the burner diameter effect upon the flashback velocity was rather negligible.

Evaluation of the laminar boundary layer thickness δ , corresponding to the turbulent flashback velocity indicates that its value must be 1.5 - 2.5 times the possible value of the so-called "penetration distance," χ , in the mixtures under consideration.

From this deduction it follows that in turbulent flow the flashback process would have to develop in the vicinity of a tube wall, namely in the boundary layer; generally speaking, visual observations confirm this.

Hence, according to the gradient-flashback theory the following equation may be obtained:

$$Re = kPr^{0.55}S^{1.11} \quad (2)$$

where $Re = \frac{wd}{\nu}$, $Pr = \frac{\nu}{\alpha}$, and ν is the kinematic viscosity coefficient.

This relation proved to be in good agreement with the experimental data mentioned above. Thus, the flashback mechanism in turbulent flow from the port is the same as the laminar flashback mechanism.

ON THE EFFECT OF KINETICS OF ELEMENTARY REACTIONS
ON IONIZATION IN STATIONARY AND NONSTATIONARY SUPER-
SONIC EXPANSION AND COMPRESSION OF GASES

STAT

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The present investigation was designed to determine the ionization ratio of the air flow, as well as the ionization ratio in the presence of an alkali metal in the air for different laws of supersonic expansion, at the initial temperatures in the adiabatic slowdown flow of $T_0 = 6000-2000^\circ\text{K}$ and initial pressures of $P_0 = 100-0.1$ atm. and for $\alpha_{\text{Na}} = 10^{-4} \div 10^{-2}$. The results of the calculations indicated significant deviation of the ionization ratio from equilibrium during supersonic expansion (in the range $1.2 \leq \beta \leq 10$ at $1 \text{ cm} \leq l_0 \leq 100 \text{ cm}$) and made it possible to determine the dependence of the limit ionization ratio upon the initial expansion parameters, the law of aerodynamic expansion and a specific size of flow l_0 . It is shown that there is a flow region for some range of β with a gradual transition of the equilibrium ionization ratio toward the freezing one, while the size of the region depends significantly on the law of aerodynamic expansion. For example, the region of transition of β for an axisymmetrical source is two or three times smaller than for a conical nozzle with a small aperture angle. The latter condition results in the fact that for flow from a supersonic source and during expansion of a supersonic stream in the vacuum, the limit ionization ratio is maximum and produces flow regions with negative dielectric constant. For the laws of expansion with slower variation of $\beta = f(l)$ during flow from nozzles and flow around a blunt body, the existence of a wide range of β with negligible deviation from the equilibrium value is typical. At the same time the limit ionization ratio is significantly less than for flow from a supersonic source. For example, for initial values of the adiabatic slowdown flow of $T_0 = 6000^\circ\text{K}$ and $P_0 = 1$ atm, the limit ionization ratio of air for a supersonic source is $2\frac{1}{2}$ or 3 times greater than for expansion with a supersonic conical nozzle $\xi = 10^\circ$. Similar relations apply in the presence of an alkali metal in the air but the limit ionization ratio in this case corresponds to higher values of β .

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