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SPONTANEOUS IGNITION AND CHAIN REACTIONS†

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I. INTRODUCTION

Our work in the field of chemical kinetics was begun about 1924 in the Electronic Chemistry Laboratory which I at that time directed in the Leningrad Physicotechnical Institute. My first coworkers were Kondrat'ev and Khariton, who were then quite young, and are now Academicians. Our group of physicists was augmented with young people and by the nineteen-thirties it had grown into the fairly large group of the Chemical Physics Institute of the Academy of Sciences of the USSR.

In 1925 we were concerned with the problem of the spontaneous ignition of gases capable of undergoing combustion and exploding. From the viewpoint of chemical kinetics, this problem was almost untouched. In any case it had never been the centre of a research effort. This situation was probably responsible for our rapid progress. In a period of 5–7 years we laid the foundations of the theory of spontaneous ignition and established that there are two and only two types of spontaneous ignition, namely: (1) thermal spontaneous ignition; and (2) chain spontaneous ignition (branched chain reactions).

I believe that this is the most important result which I and my closest associates achieved in the course of my long life.

Thermal spontaneous ignition results from the liberation of heat in exothermic reactions and the production of a thermal avalanche, since the heat liberated, and hence the increase in the temperature of the gas, leads to an increase in the reaction rate, which in turn leads to an increase in the liberation of heat and to a further increase in temperature, and so on.

Chain spontaneous ignition also results from the liberation of energy in chemical reactions, not in the form of heat, but at a stage before the energy is converted into heat. This energy being liberated leads to an increase in the number of free atoms, radicals, and electronically-excited particles with extremely high chemical activity, that is, to the development of a so-called chain avalanche. Here the increase in the temperature of the gas is a result, and not the cause, of the spontaneous ignition.

All subsequent studies in this country and abroad confirmed these conclusions, not only qualitatively, but quantitatively. Even when nuclear explosions were discovered, they were also found to be of the same two types — thermonuclear and branched-chain. Formally, the theories were also found to be similar, although they naturally differed quantitatively.

II. THERMAL SPONTANEOUS IGNITION

The earliest work (on thermal explosion) began with the development of a quantitative theory, which was subsequently verified by experiment. The history of our development of the thermal theory of explosion is extremely

† This review is based on a paper presented at the Symposium on Chain and Radical Reactions on the 11th April 1966 in the Scientists' Club, Moscow.

curious. In addition to our early work on chemical kinetics in 1923–1926, Val'ter and I were concerned with the problem of the breakdown of dielectrics. As a result of this work[1,2], we formulated the thermal theory of breakdown due to the breakdown of thermal equilibrium between the Joule heat being liberated and the heat removed from the body of the dielectric to the electrodes.

The fortunate idea that all the conclusions from the thermal theory of breakdown were applicable to the theory of spontaneous ignition or — which is the same thing — spontaneous explosion, came to us in 1927. Here the liberation of heat was associated with a chemical reaction, albeit a very slow one: $Q_1 = q_1 W$, where q_1 is the heat of reaction and W the reaction rate calculated for the entire volume of the vessel v. Thus $W = vw$, where w is the reaction rate in unit volume. In the simplest example $w = k_0 a^n e^{-E/RT}$, where k_0 is the pre-exponential term of the reaction rate constant, E the activation energy, $n = 1$ for unimolecular reactions and $n = 2$ for bimolecular reactions, and a the number of parent molecules per unit volume (if w is expressed as the number of molecules which have reacted in unit time). Thus the quantity Q_1 increases rapidly with the initial temperature of the gas T_0 according to the exponential $e^{-E/RT}$ law. The heat transfer Q_2 takes place through the walls of the vessel. For convective heat transfer we have $Q_2 = \kappa(T - T_0)s$, where T is the temperature of the gas being heated by the reaction, T_0 the temperature of the walls, and s the surface area of the vessel. The form of the expression is the same for conductive heat transfer.

Let us plot Q_1 and Q_2 as functions of temperature on the same diagram. Let us consider the example where p is constant and T_0 is variable (Fig. 1) and that where T_0 is constant and p is variable (Fig. 2). Curves *1* in both diagrams correspond to thermal equilibrium with an increase in the temperature of the gas by the small quantity ΔT. Curves *3* in both figures, for which Q_2 is always less than Q_1, correspond to there being no thermal equilibrium, that is, to the production of a thermal avalanche leading to spontaneous explosion. Curves *2*, for which the heat-transfer straight line touches the heat-production curve, separate the two regions and determine in Fig. 2 the ignition temperature T_0 at a given pressure or in Fig. 1 the ignition pressure at a given temperature T_0. At the point of tangency $Q_1 = Q_2$ and $\frac{dQ_1}{dT} = \frac{dQ_2}{dT}$.

By solving these equations, we obtain the critical condition for explosion:

$$\delta_{cr} = \frac{qvk_0 a^n Ee}{NRT_0^2 \kappa s} e^{-E/RT_0} = 1, \qquad (1)$$

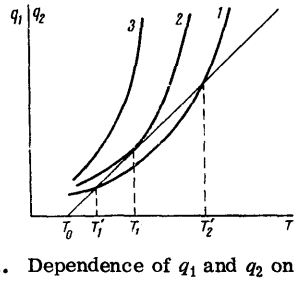


Fig. 1. Dependence of q_1 and q_2 on T (see text for explanation).

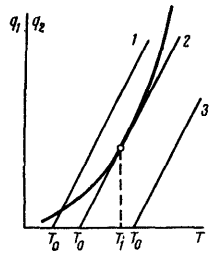


Fig. 2. Dependence of q_1 and q_2 on T (see text for explanation).

where a is expressed as the number of molecules per unit volume, and q is the molar heat of reaction.

If $\delta_{cr} \geqslant 1$, explosion will always take place, and if $\delta_{cr} \leqslant 1$, no explosion will take place.

Since $a \simeq 10^{19}(p/T)$, we can write the equation

$$\delta_{cr} = \frac{qk_0 Eevp^n \times 10^{19}}{NR\kappa s T_0^{2+n}} e^{-E/RT_0} = 1. \qquad (2)$$

For a given vessel and a given heat-transfer coefficient κ, we obtain the following relationship between the critical values of T_0 and p:

$$\log \frac{p}{T_0^{1+2/n}} = \frac{A}{T_0} + B. \qquad (2')$$

The constant B is determined by the kinetic and thermal constants and by the shape and dimensions of the vessel, and the quantity $A = 0.217E/n$. The theory was formulated in this form in my paper[3,4] in 1928. In the same year our colleague Zagulin published a paper[5] in which it was shown for the example of the spontaneous ignition of Cl_2O, that formula (2′) is confirmed experimentally.

From earlier kinetic experiments, carried out abroad, it was known that the decomposition of Cl_2O takes place by a bimolecular reaction with activation energy $E \simeq 25\,000$ cal × × mole^{-1}. Knowing the value of A, Zagulin was able to determine the value of E from explosion experiments, and in this way he obtained the same value $E = 25\,000$ cal mole^{-1}.

In 1935 Rice and Allen[6] obtained analogous verification for the example of the decomposition of azomethane. From kinetic data it was established that the reaction is unimolecular and has an activation energy of 51 000 cal mole^{-1}. In a study of the spontaneous ignition of azomethane, Rice and Allen confirmed the correctness of formula (2′) and from the value of A they found the activation energy E to be 50 000 cal mole^{-1}, in excellent agreement with the kinetic data.

These experiments convinced everyone that the thermal theory correctly takes account of the part played by kinetics in spontaneous-ignition processes. For complete confidence, however, it was necessary to show that, from a knowledge of the kinetic and thermal parameters, we were able, by applying the theory of thermal explosion, to calculate theoretically the ignition temperature for various gas pressures. This was achieved in our Institute by Frank-Kamenetskii[7], who examined the case of conductive heat transfer in a cylindrical vessel. The only change in the value of the critical parameter δ_{cr} in this example is that in

formula (2) the coefficient κ is replaced by $4\lambda/r$ and $v/s = r/2$. Substituting the values of λ, r, E, and q, Frank-Kamenetskii calculated the spontaneous-ignition temperatures of azomethane, methyl nitrite, and dinitrogen monoxide at various pressures. The calculated values were found to be very close to the experimentally determined spontaneous-ignition temperatures. This confirmed conclusively the quantitative reliability of the thermal theory of explosion[8].

Thermal explosion will always take place if $\delta_{cr} \geq 1$; this can be written in the form

$$t_r \leqslant \frac{qEt_e}{CRT_0^2}, \qquad (3)$$

where t_e is the thermal relaxation time of the system, that is, the time required to cool by a factor of e a gas heated by the reaction, C the heat capacity of the gas, and t_r the duration of the reaction, an arbitrary quantity which can be readily determined by measuring the initial reaction rate

$$t_r = \frac{d}{k_0 a^n e^{-E/RT}}, \qquad (4)$$

where a is the number of molecules per unit volume for the original fuel gas. If $t_r \geqslant \frac{qEet_e}{CRT_0^2}$, thermal ignition is impossible. If $t_r \leqslant \frac{qEet_e}{CRT_0^2}$, the fuel gas is always ignited thermally. The time t_r for a given gas pressure, that is, for a given number of molecules a in unit volume, is inversely proportional to the reaction rate close to the explosion temperature. Thus in order to determine whether an explosion is thermal in character, it is sufficient to measure the initial reaction rate at a pressure only just less than the explosion pressure, to measure or calculate the relaxation time t_e, and to estimate, even approximately, the value of the activation energy E. If the reaction rate corresponds even approximately to the expression (3), the explosion is undoubtedly thermal in character. If, however, t_r is found to be greater by one or several orders of magnitude, this is a reliable indication that the ignition is not thermal in character but is a chain process.

Until now we have restricted ourselves to simple unimolecular and bimolecular reactions. The theory can readily be generalised to more complicated kinetic laws, for example to autocatalytic reactions, chain reactions with unbranched chains, etc. The problem here reduces basically to the problem of making allowance for the more complicated kinetic laws.

We also studied experimentally the problem of the course of a thermal explosion with time. It was found that thermal explosion does not take place instantaneously, but after a certain induction period (usually of the order of one second or fractions of a second for non-autocatalytic reactions). The problem was developed theoretically by Todes[9,10], in complete agreement with experiment. This examination showed that the temperature of pre-ignition heating $\Delta T = \frac{RT_0^2}{E}$ is reached comparatively slowly, but that explosion takes place almost instantaneously when this temperature has been reached. When the thermal spontaneous-ignition temperature or pressure are much greater than the critical values and we can neglect heat transfer, we obtain from theory, for the induction period t_i, the expression $t_i = t_r \frac{CRT_0^2}{Eq}$, in good agreement with experiment.

Let us now consider the idealised case of a purely adiabatic thermal explosion, in which the heat transfer is equal to zero, and $t_e = \infty$. It can readily be seen from the criterion that thermal explosion is possible at any value of t_r, no matter how great, or, which is the same thing, at any values of the reaction rate, no matter how small. We have seen from the previous formula, however, that the induction period will then reach improbably high values. Thus if for a given fuel gas with $E = 40$ kcal mole^{-1} at a temperature $T_0 = 600$°K the induction period t_i is equal to 1 s, the value of t_i at $T_2 = 300$°K will be greater by a factor of $\exp\left[\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$, that is, the time required for thermal explosion to take place reaches millions of years. This is of course, the same result as if the explosion were impossible. If, however, the temperature is not 300° but 450°K the induction period will be equal to 14 h. The problems of predicting long induction periods for long relaxation times, particularly in the case of solid explosives, is of some practical importance. It should be noted that under given conditions these extremely long induction periods in practice retain their very precise value.

It should be noted that up to the mid nineteen-twenties the problems of spontaneous ignition and flame propagation had been examined by explosives experts, heat engineers, and to some extent by physicists and mechanical engineers. Since the time of van't Hoff, these problems had been of little interest to physical chemists. As a rule, no account was taken of chemical kinetics in problems of combustion. In its place there was introduced the concept of spontaneous-ignition temperature as a constant characteristic of each fuel. We have shown above that the spontaneous-ignition temperature is not a constant quantity. In our work, the phenomenon of combustion was based on chemical kinetics, complicated by the liberation of heat and by the existence of an inverse relationship between increase in temperature and kinetics. This was the first instance of a wider class of phenomena, now known as macrokinetics. It was on this basis that it was subsequently possible to convert not only the theory of spontaneous ignition but also the theory of various forms of flame propagation into a chapter of chemical kinetics. This principle subsequently formed the basis for the theory of flame propagation (B. Lewis, Ya. B. Zel'dovich, D. A. Frank-Kamenetskii, N. N. Semenov, and others), the concentration limits of the ignition and propagation of a normal flame (Zel'dovich), some problems of turbulent flame propagation (in particular K. I. Shchelkin), problems of the concentration limits of the detonation and combustion of powders (A. F. Belyaev and O. I. Leipunskii), etc. In recent years we have developed a theory of the spontaneous ignition of condensed explosives.

III. CHAIN SPONTANEOUS IGNITION

In contrast to thermal spontaneous ignition, the work here began not from theory but from experiment. In 1926, Khariton[11], who was occupied with problems of the extinction of the chemiluminescence of phosphorus vapour at low oxygen pressures, unexpectedly discovered that at a certain fairly low oxygen pressure, below a limiting pressure p_1, phosphorus vapour did not ignite. The vapour pressure of phosphorus (over a piece of phosphorus in a vessel at room temperature) and oxygen was so low (0.1–0.001 mmHg depending on the conditions of the experiment) that there could be no question of thermal ignition. This was also proved by direct experiment.

Moreover, phosphorus vapour undergoing combustion at $p > p_1$ is extinguished immediately as soon as the oxygen pressure falls, as a result of the oxidation of phosphorus, to a pressure only just less than p_1, although the apparatus still contains oxygen and phosphorus. If a certain quantity of inert gas (argon) is added at $p < p_1$, a flash is produced. Thus the limiting value of the partial pressure of oxygen p_1 is for some reason decreased in the presence of argon.

These observations radically contradicted the theories held at that time, since the rate of a reaction always decreases smoothly as the components are consumed, and there seemed to be no reason for the reaction to stop suddenly.

The extent to which these results of ours appeared paradoxical at that time can be seen from the criticism of the famous scientist Bodenstein [12], who was the leader in world chemical kinetics at that time. He wrote that Khariton's experiments were erroneous, and asserted that the characteristic features of Khariton's apparatus caused a diffusion stream of phosphorus oxide vapour from the reaction vessel. This stream removed oxygen from the vessel, and when the McLeod gauge (which was separated from the vessel by a trap cooled with liquid air) showed a pressure p_1 the reaction vessel in fact contained no oxygen. Later he wrote that Khariton and Val'ta were trying, in their paper, to reintroduce the ideas of the existence of so-called "false" equilibria, which had been clearly shown to be erroneous early in the nineteen-hundreds by many careful studies, including his own. This paper was therefore incorrect, like all earlier papers of this sort. In conclusion, Bodenstein did not advise anyone to concern themselves with these hopeless problems.

Bodenstein's criticism appeared convincing to my colleagues at the Physicotechnical Institute, and even to my coworkers in my laboratory. Even I lived through not a few unpleasant hours. Without delay, I undertook to verify and continue Khariton's work, and with some numerical refinements confirmed his results [13-16].

I carried out a series of experiments in which the possibility of a diffusion stream was eliminated completely; in spite of this, all the unusual phenomena reported by Khariton and Val'ta were preserved.

Conclusive proof was thus obtained for one of the most surprising phenomena in nature — the sharp transition from the almost complete inertness of a substance to its vigorous reaction, with a negligible change in its density. I would remind you that in our time the existence of a similar phenomenon has made it possible to produce energy in atomic reactors and to use atomic bombs.

Let us return, however, to late 1926 and the inoffensive experiments with phosphorus. I made a thorough quantitative study of the various regular features of the phenomenon of the lower pressure limit and its dependence on the degree of dilution with inert gas, phosphorus vapour pressure, and temperature. Shal'nikov and I discovered another surprising phenomenon — the existence of critical vessel dimensions. It was found that the critical pressure is inversely proportional to the square of the diameter d of a spherical vessel. At this point we ceased to understand anything at all. It appeared that the reactivity of phosphorus is determined not only by its density but also by what seemed to be completely unrelated parameters — the volume or dimensions of the reaction vessel. We then tried to summarise all the data which we had obtained in the form of an empirical criterion for the spontaneous ignition of phosphorus vapour (analogous to that described above for thermal explosion).

This criterion had the form

$$d^2(O_2)(P_4)\left[1+\frac{(A)}{(P_4)+(O_2)}\right]=C, \qquad (5)$$

where A represents argon and the parentheses denote the partial pressures of the corresponding gases. For cylindrical vessels, the value of the constant C was found to be about 10^{-3} when the pressure is expressed in mmHg and the diameter d of the vessel is expressed in cm.

We first suggested that the oxidation of phosphorus was a Bodenstein chain reaction with alternation of the active particles (here biradicals) — O atoms and P_4O, for example, according to the scheme:

(1) $O + P_4 \rightarrow P_4O$.
(2) $P_4O + O_2 \rightarrow P_4O_2 + O$ etc. $\qquad P_4O_2 \rightarrow P_4O_{10}$.

The oxides P_4O_2 (probably also biradicals) were rapidly oxidised further to P_4O_8 and P_4O_{10} with the liberation of a large amount of energy. Even at this stage we introduced a hypothesis which departed from that of Bodenstein. We suggested that the active particles (for example O atoms), may disappear at the walls of the vessel, by adsorption (with subsequent heterogeneous reaction, for example O + + O → O_2). The left-hand side of the empirical expression is then found to be proportional to the length of the chain ν, that is, to the number of elementary reactions (1) and (2) between the initiation of the chain and its termination at the walls of the vessel. In 1928 Trifonov [17] in our laboratory proved by direct experiment that in the photochemical chain reaction $H_2 + Cl_2$ at a pressure of about 20 mmHg chain rupture in fact takes place almost exclusively at the walls of the vessel. The reaction rate and hence the length of the chain here was found to be proportional to d^2.

These unbranched reactions, however, take place at a constant rate $n_0\nu$, where n_0 is the number of primary P_4O radicals or O atoms initiated in one second. Their number, like the length of the chain, changes smoothly with pressure, so that this suggestion does not explain the existence of the lower limit of oxygen pressure $(O_2)_1 = P_1$.

At this point an idea occurred to us.

What if, in addition to Bodenstein's unbranched chains (Fig. 3), there also existed branched chains (occasional branching as in Fig. 4 or multiple branching as in Fig. 5)? In other words, let us assume that there is a certain mathematical expectation δ that at each step in the chain an average of one new O atom is produced by the energy of the



Fig. 3. Schematic representation of an unbranched chain reaction.

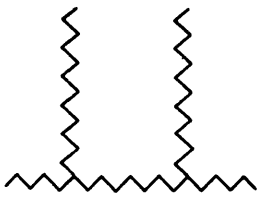


Fig. 4. Schematic represention of a chain reaction with occasional branching.

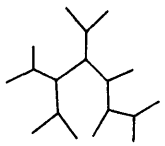


Fig. 5. Schematic representation of an intensively branched chain reaction.

oxidation of P_4O_2 to P_4O_{10}. If the branching is only occasional, δ is a small fraction. If then $\nu\delta = 1$, each act of chain termination will be compensated by the necessary production of one new chain as a result of the act of branching. When $\nu\delta > 1$ (for example, $\nu\delta = 2$), however, the number of chains will automatically increase with time, and ignition will take place. Thus the condition $\nu\delta = 1$ is the criterion for the transition from a negligible rate of reaction (with small value of n_0) to the vigorous reaction of chain ignition.

Since for each starting material the value of δ is constant, the condition $\nu = C$ is the condition for ignition; this remained to be proved.

The mechanism of the branching was still not clear. Soon afterwards, however, Leipunsky [18] passed a beam of slow electrons through phosphorus vapour burning at low pressures, and showed that the kinetic energy of the electrons increases considerably (up to 10 eV, that is, up to energies which are almost double the energy of the dissociation of oxygen into atoms). From this we concluded that in the oxidation of P_4O_2 to P_4O_{10} electronically-excited particles are produced, capable, on collision with an O_2 molecule, of bringing about the dissociation of the latter into two atoms, leading to energetic chain branching.

My paper was published in 1927. Almost immediately I received a letter from Bodenstein, in which he withdrew his objections and accepted our discovery; soon afterwards, at a meeting of electrochemists, he did this publicly. I am very grateful to Professor Bodenstein for his criticism, without which we would hardly have continued Khariton's work, and also for his subsequent systematic support of my work in this field.

A. F. Ioffe and all my colleagues in Leningrad accepted our work and congratulated us on our discovery.

In 1928 I reported the preliminary results obtained by Ryabinin [19] and myself on the chain ignition of sulphur vapour in oxygen, where the results obtained were analogous to those of the experiments on the ignition of phosphorus, and also Zagulin's results [20] on the chain ignition of $H_2 + O_2$ and $CO + O_2$ mixtures (in the last two instances the lower limit of p_1 for the mixture is observed only at a temperature above a certain critical temperature, below which no ignition takes place).

In 1928 Hinshelwood and Thompson [21] published the first results of their study of the so-called upper limit for the oxidation of mixtures of hydrogen and oxygen. Surprisingly, spontaneous ignition did not take place at pressures in the mixture greater than a certain limiting value p_2, whose magnitude decreased fairly rapidly with decrease in temperature. By combining Zagulin's data on the lower limit with Hinshelwood's data on the upper limit, it was possible to draw, on pressure–temperature coordinates, the region of spontaneous ignition in the form of a peninsula terminating in a sharp point (Fig. 6). Unlike the lower limit, the upper limit does not depend on the dimensions and state of the walls of the vessel, so long as the upper limit is not too close to the point. Hinshelwood also found that the magnitude of p_2 was influenced considerably by an inert gas, which reduced the partial pressure of the $H_2 + O_2$ mixture at the upper limit. The decrease in this partial pressure was found to be close to the partial pressure of the inert gas, so that with respect to total pressure the upper limit remained almost unchanged. The merit of Hinshelwood's work was that he interpreted the phenomenon of the upper limit within the framework of the theories of branched chain reactions. He suggested that termination at high pressures is determined by the ternary collision of the active particle with a molecule of oxygen and any other molecule M, in particular the inert gas, whereas the branching, as in the situation close to the lower limit, is determined by the binary collision of the active particle with oxygen. In this case, however, with increase in the total pressure of the mixture, the chain termination will increase in proportion to the quantity $(O_2)(M)$, whereas the branching will increase in proportion to (O_2), and at a certain total pressure p_2 the termination will become equal to the branching. At $p > p_2$, spontaneous ignition is impossible. The temperature dependence of the limiting value of p_2 is related to the activation energy of the branching process, since chain termination, which takes place on ternary collisions, involves almost no activation energy.

The chemical mechanism of the oxidation of hydrogen became known only after Lewis [22] put forward his celebrated scheme for this reaction. It was found that the branching is associated with the reaction of an H atom with oxygen: $H + O_2 \rightarrow OH + O$ followed by the rapid reaction $O + H_2 \rightarrow \rightarrow OH + H$, whereas termination in the bulk is associated with the reaction $H + O_2 + M \rightarrow HO_2 + M$. Under these conditions HO_2 is a radical with low activity, incapable of propagating the chain. For many reactions taking place at relatively low temperatures, where an important part is played by the presence of oxygen atoms, chain termination by the reaction $O + O_2 + M \rightarrow O_3 + M$ is possible, as shown by Hinshelwood and Dalton [23].

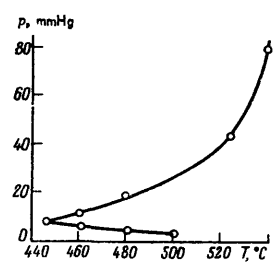


Fig. 6. Range of ignition of hydrogen [20].

Since chain termination may take place both at the walls of the vessel and within the vessel (by ternary collisions), I put forward in the early nineteen-thirties a quantitative theory of the entire field of spontaneous reactions.

In 1929 my coworkers and I showed that an analogous ignition peninsula is observed for the reaction $CO + O_2$.[20] Similar regions of chain spontaneous reaction are characteristic of many other oxidations, for example, the oxidation of phosphine[24] (Fig. 7) and silane[25] (Fig. 8).

Early in 1928, I published papers[3,4] on the two types of spontaneous reaction. The theory of thermal spontaneous reaction outlined above was described for the first time, and the first ideas were put forward regarding chain spontaneous reaction and the development of the chain avalanche.

I propose to describe here the theory of branched chain reactions in the form in which we put it forward several years later[26-29].

It can readily be seen that when one type of active particle (atoms or radicals) is present, the kinetic equation determining their concentration n is of the form

$$\frac{dn}{dt} = n_0 + (f - g)n, \qquad (6)$$

where fn is the rate of the branching reaction, gn the rate of chain termination, and n_0 the number of active centres produced in one second as a result of thermal motion. At constant concentrations of the original gases or at the start of the reaction, when combustion can be neglected, f and g are constant quantities. At low pressures, when the disappearance of the active centres is determined by their capture by the walls of the vessel, the value of g (for a probability ϵ of capture by the wall equal to 1) for cylindrical vessels is given by the equation

$$g = \frac{25.2D_0}{d^2p},$$

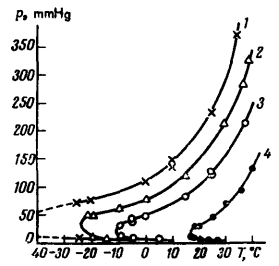


Fig. 7. Range of ignition of phosphine[24]: 1) 57% PH_3; 2) 43% PH_3; 3) 22% PH_3; 4) 10% PH_3.

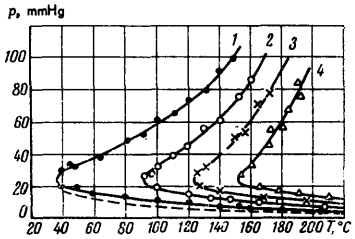


Fig. 8. Range of ignition of silane[25]: 1) 49% SiH_4; 2) 39% SiH_4; 3) 30% SiH_4; 4) 14% SiH_4.

where D_0 is the diffusion coefficient of the active centres at p = 1 mmHg, and d the diameter of the vessel. At very low values of ϵ we have $g = \epsilon u/d$, where u is the thermal velocity of the active particles. The values of g for intermediate values can be found from papers published by Lewis and myself. By treating the walls of a glass or quartz reaction vessel with various substances or in other ways, it is possible to vary the value of the limit p_1 over a wide range (by a factor of up to 100) for a given diameter.

As a rule, in all chain reactions we are dealing with not one but several (a minimum of two) active centres (for example P_4O and O), and hence we are dealing with not one but two or several kinetic differential equations. Usually, however, one of these active particles reacts much more slowly than the other, and this makes it possible, with a certain degree of approximation, to reduce the system of differential equations to one differential equation, which describes the change in the concentration of this least active centre, whose concentration is much greater than that of the others. Then, of course, the constant f becomes a complex quantity including the reaction rate constants of all the centres. By integrating Eqn. (6), we obtain:

$$n = \frac{n_0}{f-g}(e^{(f-g)t} - 1) = \frac{n_0}{\varphi}(e^{\varphi t} - 1) \quad \text{for } (f-g) = \varphi > 0, \qquad (7)$$

$$n = n_0 t \quad \text{for } (f-g) = \varphi 0, \qquad (8)$$

$$n = \frac{n_0}{g-f}(1 - e^{-(g-f)t}) \quad \text{for } (f-g) = \varphi < 0. \qquad (9)$$

The equality $f = g$ is simply the criterion determining the limit. For $f > g$, the concentration of active centres increases exponentially with time. The reaction rate $w_t = kn$ (where $1/k$ is the mean time required for the active centre to react with the original molecule) increases according to the same exponential law. The quantity of substance x which has reacted at moment of time t also increases exponentially with time: $x_t = \int_0^t w_t dt$. For infrequent chain branching we have $k \gg f$, and for intensive chain branching we have $k = f$. Subsequently, we shall consider the development of chain branching at pressures which are only slightly greater than the lower limit, since at these pressures, as a result of the high thermal conductivity, the increase in the temperature of the mixture during the reaction is small.

Close to the lower limit, $\frac{g}{f} = \frac{p_1}{p_0}$, where p_1 is the pressure of the lower limit, and p_0 the original pressure of the mixture above the lower limit.

It follows from formula (7) that the reason for the chain avalanche is the rapid increase in the number of active centres capable of reacting. Even at low pressures, exceeding the lower limit by a factor of only 1.5–2, the value of f is very large and varies from several tens to several hundred reciprocal seconds. Thus the development of the reaction with time takes place within tenths or even hundredths of a second.

For $f < g$ the reaction rate is always less than the quantity $n_0 t$ and soon reaches a steady value (in the absence of appreciable combustion) $w = kn = \frac{kn_0}{g - f}$ or (for intensive chain branching, when $k \simeq f$):

$$w = \frac{n_0}{(g/f - 1)} = \frac{n_0}{p_1/p_0 - 1}, \qquad (10)$$

where $p_0 < p_1$ (for $f < g$).

Thus the characteristic feature for branched reactions taking place under the limit is a rapid increase in rate, which does not correspond to the increase for ordinary reactions, as the limit is approached (Fig. 9). For $p_1/p_0 = 1$, the rate naturally does not tend towards infinity, but reaches values kn_0t, that is, it begins to increase linearly with time. The closer we are to the limit, the greater the time required for the steady rate to be reached. Even for $\frac{g}{f} - 1 = 0.01$, however, that is, when the value of p_0 is only 1% less than p_1, the reaction rate will in practice reach a steady state within one second.

In order to show clearly the change in the reaction rate w and the quantity x of substance reacted as a function of time, we can construct, for intensive chain branching with $n_0 = 10^3$, $f = 500$, and different values of the ratio p_1/p_0, corresponding curves for the quantity x, on a smaller scale for $f > g$ and on a much larger scale for $f < g$ (Figs. 10 and 11).

It should be noted that the quantity n_0, that is, the rate of spontaneous initiation of the primary radicals, is relatively very small. In actual fact, this process is associated with the production of the primary active particles — free atoms and radicals — from neutral molecules under the influence of thermal motion. Almost no thermal dissociation of the original molecules to give two free atoms or radicals takes place at room temperatures. The production of free radicals as a result of reaction between the original molecules, for example, $P_4 + O_2 \rightarrow P_4O + O$ or $H_2 + O_2 = 2OH$, has a much higher probability. Even these processes, however, are associated with a fairly large activation energy, so that n_0 is always small. It should, however, be noted, that the growth of the chain avalanche takes place so rapidly that the appearance of only a few primary active particles is sufficient to lead to their production in vast quantities within one second.

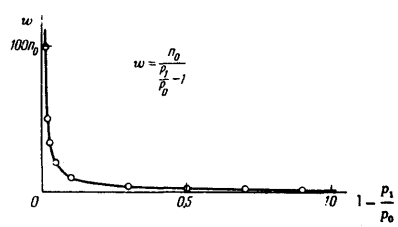


Fig. 9. Dependence of w on p_1/p_0 (for $f < g$).

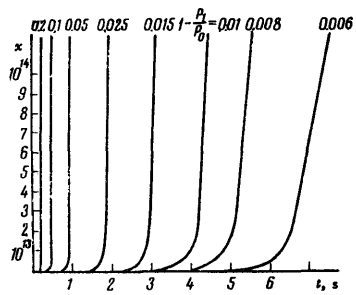


Fig. 10. Dependence of x (quantity of substance reacted) on t at various values of p_1/p_0 (n_0 = $= 10^3$ mole cm^{-3} s^{-1}; for $f > g$; $f = 500$ s^{-1}).

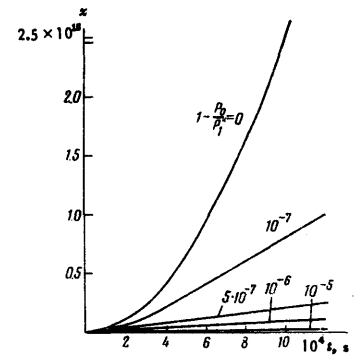


Fig. 11. Dependence of x on t at various values of p_1/p_0 ($n_0 = 10^3$ mole cm^{-3} s^{-1}; $f < g$).

It is possible in principle, however, to have instances where even one active centre is produced very rarely. We encountered such a case in a study, with Ryabinin[19], of the ignition of sulphur. Above the lower limit here ignition took place only rarely, and usually no ignition was observed. When a weak discharge was passed through the cylinder containing the oxygen, however, and the oxygen was then passed into the vessel containing the sulphur, ignition was always observed above the lower limit.

We would remind you that in atomic bombs a neutron source is used for the same purpose.

Since the value of n_0 is always very small (at a pressure $p \leqslant p_1$), the reaction rate is equal to almost zero and conditions for the development of a chain avalanche are not created. At a pressure only slightly greater than p_1 the reaction rate increases rapidly to extremely high values within a fraction of a second.

The first experimental verification of the theory of branched chain ignition was obtained in our Institute by Koval'skii[30] for the example of the oxidation of detonating gas ($2H_2 + O_2$) at 485° and various p_1/p_0 ratios (Fig. 12). From this it was possible to determine the value of f and hence the branching constant[31]. The exponential growth of the avalanche is confirmed up to a degree of conversion of 20–30% (Fig. 12). The curves for high degrees of conversion are distorted because of the decrease in the concentration of the original gases. A complete analysis of

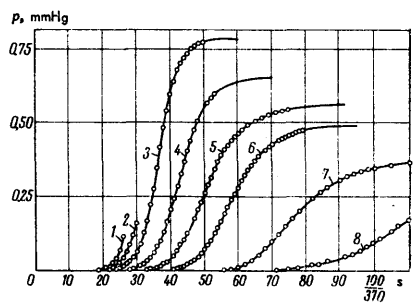


Fig. 12. Kinetics of the oxidation of a $2H_2 + O_2$ mixture at 485° and various initial pressures (mmHg): 1) 8.2; 2) 7.8; 3) 7.4; 4) 7.1; 5) 6.8; 6) 6.4; 7) 6.1; 8) 5.8.[30]

the curves for the development of the chain avalanche was made difficult by the lack of reliable data on the chemical mechanism of the reaction. The experimental verification of the theory became much easier after Lewis[22] put forward his scheme for the oxidation of hydrogen.

When applied to a pressure near the lower limit, this scheme for the oxidation of hydrogen, for which rigorous experimental verification was subsequently obtained, can be written in the form:

(1) $OH+H_2 \rightarrow H_2O+H$,
(2) $H+O_2 \rightarrow OH+O \rightarrow$ chain branching,
(3) $O+H_2 \rightarrow OH+H$,
H+ wall, O+ wall, OH+ wall $\rightarrow$ chain termination.

It is assumed that the chains are initiated by the reaction $H_2 + O_2 \rightarrow 2OH$. The smallest reaction rate (particularly when the mixture contains an excess of hydrogen) is that of the reaction $H + O_2 \rightarrow OH + O - 17$ kcal. This is the only endothermic step. From this it was concluded that in mixtures with an excess of hydrogen over the stoichiometric quantity, the highest concentration in the course of the reaction will be attained by H atoms. By using the method of quasi-steady concentrations for the change in the concentration of H with time, we obtain the expression:

$$\frac{d[H]}{dt} = n_0 + (2a_2 - a_2')[H] = n_0 + 2a_2\left(1 - \frac{a_2'}{2a_2}\right)[H], \qquad (11)$$

where $f = 2a_2 = 2k_2[O_2]$; $g = a_2'$; $n = [H]$; and $(1 - a_2'/2a_2) = (1 - p_1/p_0)$.

We can also write a differential equation for the rate of consumption of oxygen:

$$\frac{d[O_2]}{dt} = n_0 + k_2[O_2][H]. \qquad (12)$$

By solving the system of differential equations (11)–(12), we can calculate the entire course of the reaction from its initiation to complete combustion. I published this work in 1944.[32] Nalbandyan and Karmilova[33] in 1958 repeated Koval'skii's experiments[30] on the study of the value of Δp as a function of t, much more extensively and in much more detail. From these experiments it was possible to determine the constant k_2 for the branching reaction, and then to compare with experiment all the theoretical relationships which I had obtained. The agreement was found to be exceptionally good. Here it was also shown that the ratio $f/g = 2a_2/a_2'$ is in fact equal to p_0/p_1. It was also shown[32] that in the reaction $2H_2 + O_2$ at $p_1/p_0 = 0.5$, the concentration (or partial pressure) of H atoms at 50% consumption of the original oxygen should amount to 30% of that of the original oxygen and hence to 60% of the reacted oxygen, or 30% of the partial pressure of the water formed. Correspondingly, at $p_1/p_0 = 0.25$ the pressure of H atoms at the maximum will amount to 80% of that for the original oxygen, and at $p_1/p_0 = 0.7$ to about 10% of that of the original oxygen (Fig. 13). All these relationships are observed at a temperature of about 500°, when there is almost no equilibrium dissociation of water. This quite surprising result could essentially have been obtained from our theory ten years earlier.

When chain termination is neglected, the result of Lewis' three elementary reactions can be expressed by the following stoichiometric relationship: $H + 3H_2 + O_2 = 3H + 2H_2O +$ + 13 kcal or $3H_2 + O_2 \rightarrow 2H_2O + 2H$. We see that the chemical energy liberated in the formation of water according to

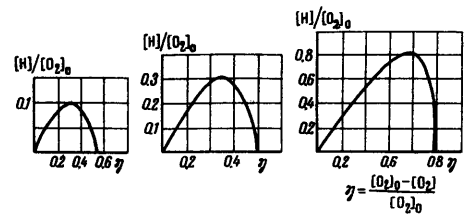


Fig. 13. Dependence of [H] on $\eta = \frac{[O_2]_0 - [O_2]}{[O_2]_0}$ at various values of p_1/p_0.[32]

the reaction $2H_2 + O_2$ is used up in the dissociation of H_2, thus maintaining the rapid development of the chain avalanche. At the end of the reaction, all the H atoms naturally recombine on the wall of the vessel, forming H_2 or H_2O molecules. This is accompanied by the liberation of an additional quantity of energy. A process taking place with the build-up of an atomic H concentration equal to twice the concentration of the original oxygen could in principle be carried out in vessels with a large radius (for example 10 m) with walls treated in such a way that the value of ϵ was very small. Here the pressure p_1 would be negligibly small, of the order of several ten-thousandths of a millimetre, and by carrying out the experiment at a pressure of say 0.1 mmHg, chain termination at the walls and within the vessel by ternary collisions $H + H + M \rightarrow$ $\rightarrow H_2 + M$ could be neglected. Then the rate at which the rapidly-formed atomic hydrogen disappeared as a result of chain termination in the interior of the vessel and at the walls would be so slow that at the end of the reaction we would have in the vessel as many H atoms as water molecules. This would make it possible to use this method of preparing atomic hydrogen for all sorts of reductions, for example, the reduction of oxides. The practical utilisation of this reaction is hindered by the fact that the pressures in the system are too low. An increase in the pressure to 10 mmHg, which would increase the quantity of atomic hydrogen by a factor of 100, would require such rapid rates of flow that the atomic hydrogen could not be prevented from recombining by ternary collisions.

This surprising conclusion regarding the vast relative concentrations of atomic hydrogen was confirmed experimentally by Kondrat'eva and Kondrat'ev[34]. They determined the concentration of free atoms from the increase in temperature recorded by a thermocouple placed in detonating gas burning at a pressure slightly greater than p_1, and confirmed the theoretical conclusion that the concentration of atomic hydrogen reaches 20–30% of the original concentration of oxygen in the mixture. Kondrat'ev's method, however, was nevertheless not quite a direct method of chemical analysis. The theory was subsequently confirmed thanks to an idea of Voevodskii's. In ordinary chain reactions the concentrations of atoms and radicals are too low to permit their detection by the EPR method. In branched chain reactions, however, where these concentrations are incomparably greater, the EPR method can be used successfully, as proved experimentally by Voevodskii and coworkers[35]. The method made it possible to determine not only the quantity of free radicals, but also their chemical composition. In 1960 Voevodskii showed that the concentration of atomic hydrogen does in fact reach the values indicated above.

Subsequently, Kondrat'ev and Nalbandyan[36], using the same method, detected considerable quantities of atomic oxygen in the $H_2 + O_2$ flame; the concentrations were found to be greatest in mixtures poor in hydrogen. Soon afterwards, the same authors[37] were able to record the EPR signals of OH radicals in the hydrogen flame and to determine their concentrations at various compositions of the mixture (Fig. 14). In the stoichiometric mixture the values of [H] reach 10^{16} molecules cm^{-3}, that is, about 1 mmHg. Earlier, it had been assumed (on the basis of the values for the rate constant of the reaction $O + H_2 \rightarrow OH + H$, given by Harteck and Kopsch[38]), that the concentration of O atoms was much smaller, by about 2 orders of magnitude, than that corresponding to the above observations. The value for the rate constant of the reaction $O + H_2 \rightarrow OH + H$, recently determined by Azatyan[39,40] by the method of limits, shows good agreement with the observed concentrations of atomic oxygen. The values of the concentration of OH radicals measured by the EPR method also agree with the value of the rate constant for the reaction $OH + H_2 \rightarrow H_2O + H$, determined by Avramenko[41] and Kondrat'ev[42].

The EPR method was also applied to the oxidation of carbon monoxide. Nalbandyan and coworkers[43-47] made a detailed study of rarefied carbon monoxide flames with oxygen in the presence of small quantities of substances acting as hydrogen donors. (Absolutely dry mixtures of CO and O_2 containing no hydrogen donors are incapable of spontaneous ignition.) H_2 and other donors were used as additives. In complete accordance with the chain branching mechanism, the combustion of CO in the presence of H_2 can be represented by the following scheme:

$$H_2+O_2\rightarrow 2OH \quad \text{(chain initiation)},$$
$$OH+CO\rightarrow CO_2+H,$$
$$H+O_2\rightarrow OH+O,$$
$$O+H_2\rightarrow OH+H,$$
$$\left.\begin{matrix} H+\text{wall} \\ O+\text{wall} \\ OH+\text{wall} \end{matrix}\right\} \rightarrow \text{chain termination}.$$

In a rarefied flame of this mixture in the presence of small quantities of added H_2, Nalbandyan and coworkers were able to detect high concentrations of atomic oxygen, hydrogen, and OH radicals, whose concentrations were found to be in good agreement with the OH concentrations previously measured by Kondrat'ev[41,42,48-50] from the electronic absorption spectra. Thus all the types of active centre assumed to be responsible for chain branching in this system were identified.

When small quantities of H_2 were added, O atoms predominated in the flame, and when large quantities of H_2 were added, H atoms predominated in the flame (see Fig. 15, which gives the concentrations of H, O, and OH for the same $CO + O_2$ mixture containing different quantities of added H_2). The concentrations of H and O atoms were always much greater than the concentration of OH radicals[51]. In the Institute of Chemical Physics of the Academy of Sciences of the USSR, Azatyan and coworkers[39,40] put forward a method for determining the rate constants for the reaction of atomic oxygen and hydrogen with the molecules of various substances, making use of the decrease in the lower limit of spontaneous ignition for the combustion of a mixture of CO and O_2 in the presence of small quantities of added H_2 or other hydrogen donors.

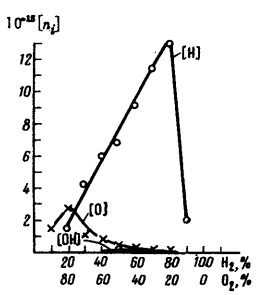


Fig. 14. Dependence of the concentrations of H, O, and OH on the initial composition of the hydrogen–oxygen mixture[37].

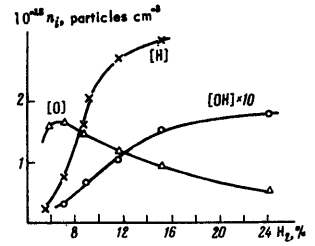


Fig. 15. Dependence of the concentrations of H, O, and OH on the initial concentration of H_2 in the CO flame[51].

This method was used to determine the values of the rate constants for all the fundamental elementary reactions in rarefied flames of hydrogen and carbon monoxide. Using these constants, it was possible to calculate by means of an electronic computer the time dependence of the concentrations of H_2O and OH during the reaction and to compare the results with the experimentally observed (by the EPR method) changes in the concentrations of all the active particles with change in the flow velocity[52]. The flow velocity can be regarded as a quantity corresponding to the reaction time. Fig. 16 gives the calculated (on the left) and experimental (on the right) values of the change in the concentrations of O, H, and OH in the flame for a $CO + O_2 + 6\%$ H_2 mixture, and shows that the curves are of similar shape. The discrepancy of 20% in the absolute values of the concentrations ought to be attributed primarily to the difference in the conditions of reaction in a flow system (in which the experiments were carried out) and the static system assumed for the calculations. The discrepancy is evidently related chiefly to the fact that no allowance was made for the diffusion of atoms in the flow system.

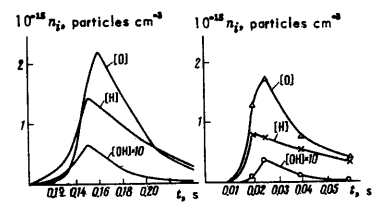


Fig. 16. Comparison of the time dependences of the concentrations of O and H atoms and OH radicals in the $2CO + O_2 + 6\%$ H_2 flame, obtained by calculation (on the left) and by experiment (on the right).[52]

TABLE. $H_2 + O_2$ mixture. p = = 2.96 mmHg, T = 993°K.

	H	O	OH
$10^{-16}(n_i)_{exp}$	6	0.8	0.16
$10^{-16}(n_i)_{theor}$	6.2	0.81	0.15

The calculated and experimental values of the H, O, and OH concentrations for an $H_2 + O_2$ mixture are given in the Table [53] (for the same interval). Such good agreement is probably accidental.

It is important to apply the EPR method to the study of the mechanism of other branched reactions, such as the combustion of phosphorus, sulphur, carbon disulphide, etc. Work in this direction has only begun to develop in our Institute.

I now wish to turn to work, carried out recently in our Institute, which has extended considerably our ideas on branched chain reactions and has shown that the number of reactions with a branched-chain mechanism is much greater than was previously supposed.

As already shown, branching is always associated with utilisation of the energy of the chemical reaction. At an early stage in the development of the chain theory [16,26], I imagined that branching takes place as a result of the formation, in the course of the reaction, of energetically excited particles, with an excess of vibrational or electronic energy, which could give up the excitation energy to molecules of the starting materials, leading to their dissociation into atoms and radicals.

Although these ideas gave a consistent and extremely general explanation for the course of branched chain reactions, the idea that excited particles take part in the branching was in fact left aside and until recently was almost never discussed in the literature.

In fact, according to modern physical theories, the simultaneous transfer of several quanta of vibrational energy when particles collide is extremely improbable.

Although the transfer of energy from electronically--excited molecules is possible, the probability of formation of electronically-excited particles in chemical reactions is generally very low.

Moreover, as we saw for the example of the oxidation of hydrogen, branching in this reaction takes place without excited particles, by the reaction $H + O_2 \rightarrow OH + O$ followed by $O + H_2 \rightarrow OH + H$. Thus it would seem that branching involving excited particles is impossible or unlikely. Nevertheless, in order to explain many phenomena observed in chain reactions, particularly in fluorination, it has in recent years become necessary to return again to the idea that a part in branching is played by energetically-excited particles, products of the exothermic elementary reactions of chain propagation.

An important addition to the old ideas, however, is the observation that the branching takes place not by the transfer of energy from an excited product molecule to a molecule of the original reagent, but by chemical reaction of the excited product molecule with the formation of atoms and radicals.

This chemical reaction may be either unimolecular decomposition of the excited molecule or its bimolecular reaction with a molecule of the original reagent.

I shall explain this with reference to several examples of fluorination, studied in Shilov's laboratory [54] in our Institute.

One of the stages in chain fluorination is the reaction

$$R+F_2 \rightarrow RF+F.$$

This reaction is so exothermic that the heat of the reaction sometimes exceeds the energy of the weakest bond in the RF^* molecule being formed. This molecule may therefore undergo unimolecular decomposition with the formation of atoms and radicals, leading to chain branching. For example, in the reaction of fluorine with methyl iodide, the chain is propagated according to the reactions

$$\text{(a) } F+CH_3I \rightarrow HF+CH_2I,$$
$$\text{(b) } CH_2I+F_2 \rightarrow CH_2FI^*+F.$$

The energy of the C–I bond in the CH_2FI^* molecule is less than the heat of reaction (b). The CH_2FI^* molecule may therefore dissociate immediately after its formation:

$$CH_2FI^* \rightarrow CH_2F+I$$

and the CH_2F radical reacts further with F_2:

$$CH_2F+F_2 \rightarrow CH_2F_2+F.$$

When fluorine is mixed with methyl iodide, flames are produced immediately, even at very low pressures of the reagents. The probability of branching is apparently so high that the range of spontaneous reaction extends over all pressures attainable in practice.

The most important proof of this mechanism was provided by the discovery of high concentrations of I atoms in the reaction zone by the EPR method. It was shown that the concentration of I atoms reaches more than 10% of the concentration of original F_2. [55] At the same time there is almost no increase in temperature in the reaction zone (the reaction is carried out at very low pressures).

An interesting feature is that whereas in the gaseous phase the reaction of CH_3I with F_2 takes place very readily, and iodine is liberated in accordance with the proposed mechanism, fluorine does not liberate iodine from methyl iodide in solution in an inert oil. This means that in the reaction there is still in principle an upper limit, produced by loss of energy from the excited CH_2FI^* molecules on collision with surrounding molecules [56].

The kinetics of the reaction of fluorine with methyl iodide were recently calculated theoretically on an electronic computer on the basis of elementary stages including the proposed branching reaction. The data obtained for the composition of the products at different reagent ratios showed good agreement with experiment.

Another type of branching reaction is observed in the addition of fluorine to alkenes. For example, in the fluorination of tetrafluoroethylene, the C_2F_5 radical produced by the addition of an F atom to the alkene may undergo unimolecular decomposition with rupture of the C–C bond according to the reactions

$$F+C_2F_4 \rightarrow C_2F_5^* \rightarrow CF_3+CF_2.$$

In actual fact, the overall heat of these two reactions is positive and amounts to ~ 20 kcal mole^{-1}, that is, the heat of the first reaction is sufficiently great to ensure subsequent dissociation of the radical. This leads to branching,

since the reaction of CF_2 with F_2 leads to the formation of two new F atoms:

$$CF_2+F_2\rightarrow CF_3+F,$$

$$CF_3+F_2\rightarrow CF_4+F.$$

A flame is readily produced when fluorine is mixed with tetrafluoroethylene. In accordance with the mechanism of a chain-branched reaction, very large concentrations of F atoms were detected in the reaction zone during the fluorination of C_2F_4.

If the excitation energy of the radical formed by the addition of the F atom to the alkene is insufficient to bring about its decomposition, branching may take place as a result of its subsequent reaction with F_2. The two successive reactions lead to the accumulation of sufficient energy for unimolecular decomposition of the resulting molecule, leading to branching.

Study of the gas-phase reactions of fluorine with tetrachloroethylene and dibromoethylene by the EPR method showed that very high concentrations of F and Cl atoms are formed in the reaction zone for the first compound, and very high concentrations of F and Br atoms in the second, confirming the suggestion that these reactions are branched chain reactions.

When the excitation energy is insufficient for unimolecular dissociation of the bond, branching may take place by the bimolecular reaction of an excited molecule of the reaction product with a fluorine molecule. The mechanism of formation of the radicals in the bimolecular reaction of valency-saturated molecules is less usual than unimolecular decomposition of a molecule, so that I would like to remind you of it at this stage.

In 1954, I suggested[29] that the activation energy of the endothermic reaction $RX + IR \rightarrow R + XI + R - q$ is close to the endothermicity q, and that its activation barrier is close to zero.

In reality, examination of the reverse reaction, in which two R radicals attack the XI molecule, indicates that its activation barrier is probably even smaller than that for the reaction $R + XI \rightarrow RX + I$, and we know that the activation barrier for reactions of radicals with molecules usually does not exceed a few kilocalories per mole. From the principle of detailed balance, it follows that the reaction of two molecules with the formation of two radicals will also have a low activation barrier.

These ideas were confirmed theoretically for the simplest reaction of two hydrogen molecules:

$$H_2+H_2\rightarrow H+H_2+H.$$

In addition, special experiments were carried out in our Institute to record radicals directly by the EPR method for those instances where the consumption of energy in the reaction is small.

Molecular fluorine is an example of a molecule for which bimolecular reactions of the type $F_2 + HR \rightarrow F + HF + R$ are particularly favourable, since they do not involve the consumption of a large amount of heat and may even be exothermic. Most chain fluorination reactions are initiated thus[57].

The activation energy of these reactions is apparently always less than the excitation energy of the molecules formed in the exothermic reactions of chain fluorination. Thus the same bimolecular reaction involving the formation of radicals from two molecules may also take place in the branching. The excited molecules of the product may react with F_2 without any additional activation energy, and this makes chain branching possible.

The simplest example is the fluorination of hydrogen. In this case, in the chain analogous to the Nernst chain for the reaction of hydrogen with chlorine: $F + H_2 \rightarrow HF + H$; $H + F_2 \rightarrow HF + F + 98$ kcal; the second reaction is exothermic to the extent of 98 kcal; this is more than twice the energy of the F–F bond.

The reaction

$$F_2+HF\rightarrow F.\,.\boxed{F\ldots H}.\,.F\rightarrow F+HF+F-38\text{ kcal}, \qquad (I)$$

requires the consumption of 38 kcal, corresponding to the dissociation energy of fluorine. It may be assumed that the greater part of the HF* molecules formed in the elementary act $H + F_2 \rightarrow HF + F + 98$ kcal will carry the greater part of the energy of this reaction, for example, 60 kcal. This is much greater than the energy consumption and corresponds to the activation energy of process (I).

Thus here branching takes place by the reaction of an excited HF* molecule with F_2. The results of experiments confirm this suggestion. It was found that the range of spontaneous reaction between hydrogen and fluorine is bounded by clearly defined upper and lower pressure limits, and this is one of the characteristics of a branched chain reaction[58].

It should be noted that the reaction of fluorine with hydrogen has always appeared puzzling, and different authors have obtained extremely contradictory results.

Thus Eyring and Kassel[59] stated that although a mixture of hydrogen and fluorine explodes readily, they were able to prepare mixtures which were stable at room temperature and a total pressure of the reagents equal to atmospheric pressure.

Others (Grosse and Kirschenbaum[60]) attributed these results to experimental errors and showed that a mixture of hydrogen and fluorine always ignites at room temperature.

Consideration of the mechanism of chain ignition indicates that these contradictions are apparently due to the fact that the first authors worked with mixtures inside the ignition peninsula whereas the others worked outside this peninsula. It should also be noted that chain termination within the interior of the vessel takes place by reaction with oxygen, so that the position of the upper limit depends to a marked extent on the concentration of oxygen impurity in the fluorine.

In all these examples it can be seen that the excited molecules of the product do not transfer energy to the original molecules. At the same time it is this energy which is used directly in the chemical reactions leading to the formation of atoms and radicals which begin new chains, so that it brings about branching in this way. Thus the old ideas of the important part played by excited molecules in branching find application here. In this connection it may be noted that in any exothermic reaction of an atom or radical with a molecule, the molecule of the reaction product initially has considerable vibrational excitation energy. A number of instances have been recorded where the greater part of the energy of the reaction is concentrated in vibrational degrees of freedom of the molecule.

Data on the dissipation of vibrational energy show that this process takes place fairly slowly according to the same principle (of which mention was made earlier) — the low

probability of multi-quantum transitions — and, which is most important, for large vibrational quanta the transfer of even one quantum usually requires 10^3–10^4 collisions.

Even in the light of the above discussion, however, we would not expect that the probability of branching would be close to unity, that is, that the chain branching would be intensive. For a chain avalanche to develop, however, it is sufficient that there be more than one branching in the total length of the chain, that is, that the probability of branching be greater than $1/\nu$. Since the lengths of the main chains in such reactions are very great, at least from hundreds to tens of thousands, this order of probability of branching is sufficient to ensure a mechanism of developing chain avalanche.

The probability of branching is determined to a considerable extent by the energy liberated in the elementary reactions of chain branching. It is therefore not surprising that so many branched chain processes have been discovered in gas-phase reactions of molecular fluorine, for which the elementary reactions are particularly exothermic. We may justifiably say that chain gas-phase fluorination is almost entirely associated with the range of branched chain reactions.

Other branched-chain reactions which have been well studied are those involved in gas-phase oxidation by molecular oxygen. Here also, branching is brought about by chemical energy, as a result of the formation of stable H–O and C–O bonds, the O–O bond being comparatively weak. The elementary processes here are less exothermic than in fluorination, so that in the gaseous phase we have both branched reactions and unbranched (or degenerately-branched) chain reactions.

Branched chain reactions are not restricted to oxidation and fluorination, however. It is known, for example, that the decomposition of NCl_3 to N_2 and Cl_2 is a branched-chain process exhibiting an upper limit[61]. The energy for branching here is undoubtedly provided by the very high bond energy in the N_2 molecule formed (225 kcal mole^{-1}). In this connection, other reactions involving decomposition with the liberation of N_2 ought to be studied. It is possible that the example of NCl_3 is not an exception.

There are other examples of chain reactions where the chain-branching hypothesis explains the observed relationships. Thus clearly defined limiting phenomena are observed in the chlorination of acetylene, according to data obtained by Shtern (in this country) and Porter (in England). It should be noted that a particularly large amount of energy is liberated in the chlorination of acetylene compared with the chlorination of other compounds.

Finally, flashes of cold flame are observed at certain pressures and temperatures in the gas-phase nitration of alkanes, as shown by Shtern[62]. Here also, a unique part is played by the formation, in the course of the elementary exothermic act, of a product which contains an excess of energy and is therefore able to undergo unimolecular decomposition with the formation of radicals.

Thus the liberation of various forms of energy in chain reactions is used to accelerate these reactions, creating the conditions for an explosion. The energy concentrated in individual molecules in the form of vibrational or electronic excitation is used for branching in chain spontaneous ignition.

This principle of the utilisation of the energy of a chain reaction can be examined on a much wider basis and applied to molecules possessing considerable chemical energy. The intermediate formation of molecules, such as peroxides and aldehydes, which are not excited but possess a considerable reserve of chemical energy relative to the final reaction products (for example, CO_2 and H_2O), may give slow branching, as a result of their kinetic instability, a phenomenon which I have named "degenerate branching".

A very large number of gas-phase and liquid-phase oxidations are known to take place by a mechanism involving these degenerately-branched chain reactions.

In conclusion, I would like to report some results on unbranched polymerisation reactions at low temperatures.

In 1960–1961 Enikolopyan, Gol'danskii, and coworkers[63] in the Institute of Chemical Physics of the Academy of Sciences of the USSR, and later other workers[64,65], in other institutes in this country and abroad, showed that in the solid-phase polymerisation of a number of monomers (acrylonitrile, vinyl acetate, methyl methacrylate, formaldehyde, etc.) under the influence of electrons with an energy of 1.5 MeV, the reaction rate is independent of temperature over a wide range of irradiation temperatures (reaching 77°K). The dependence of the initial rate of polymerisation of acrylonitrile on the reciprocal of the temperature is shown in Fig. 17. It can be seen that the rate of polymerisation in the liquid phase decreases with decrease in temperature in accordance with a value for the activation energy E = 3000 cal mole^{-1}, but at the freezing point (m.p. = 355°K) the rate increases by a factor of 25 and subsequently remains unchanged down to 77°K. In other words, the effective activation energy in the solid phase is zero. Generally speaking, on going from the liquid to the solid phase, the rate may increase considerably (acrylonitrile and formaldehyde), decrease considerably (methyl methacrylate), or remain almost unchanged (vinyl acetate)[63]. The striking feature always, however, is that the rate is constant over a wide temperature range in the solid phase, from 77°K to the melting point.

It is now known that many other monomers polymerise in the solid phase with zero activation energy.

Other forms of polymerisation temperature dependence are also known. For example, almost no polymerisation of hexamethylcyclotrisiloxane (HMCTS) takes place in the liquid phase, but the rate of the process increases sharply as the freezing point is approached, reaches a maximum in the solid phase close to this point, and with further decrease in temperature the rate again decreases and gradually reaches a plateau which extends down to 77°K (Fig. 18).

In the polymerisation of phenylacetylene there is no sharp change in activation energy on passing through the melting point (Fig. 19)[63], and with decrease in temperature the reaction rate continues to decrease slowly, showing only a slight tendency to form a plateau close to 77°K.

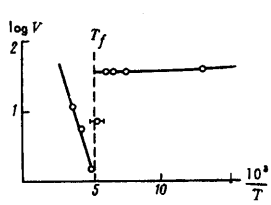


Fig. 17. Temperature dependence of the rate of polymerisation of acrylonitrile[63].

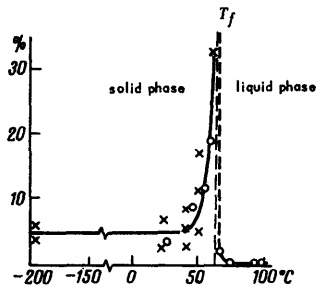


Fig. 18. Temperature dependence of the rate of polymerisation of hexamethylcyclotrisiloxane [63].

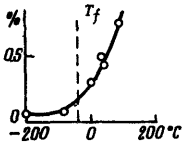


Fig. 19. Temperature dependence of the rate of polymerisation of phenylacetylene [63].

There remained doubts, however, as to whether the polymerisation takes place during the irradiation of the specimen or only during its subsequent treatment (de-freezing and isolation of the polymer). To investigate this problem, Barkalov and coworkers [66] used a special calorimeter to record the thermographic thawing curves as vinyl acetate, which had previously been irradiated at -196°C, was gradually heated. Two heat-liberation peaks were detected, close to the temperature of the phase transformation of vinyl acetate at -129°C and close to the melting point at -93°C. The same experiment was carried out without any irradiation. The thermographic curves obtained in the two experiments practically coincided, showing that no polymerisation takes place under the conditions of thawing. If polymerisation had taken place during thawing, the curves from the two experiments should have been different, because of the additional liberation of the heat of polymerisation in the first experiment.

Barkalov and coworkers [67], using a specially constructed differential thermocouple, made direct measurements of the heat liberated during the irradiation of acrylonitrile at -196°C, and hence the rate of polymerisation and the total quantity of heat liberated. It was found that the rate of polymerisation and the total quantity of heat are very close to those from the kinetic curves measured from the yield of polymer after thawing. This proved that the entire polymerisation took place at low temperature directly under the influence of the beam. Unfortunately, it was possible to carry out only a few of these experiments because of the destruction of the calorimeter.

In France, Bensasson and Dworkin [68], in Magat's laboratory, repeated the experiments with acrylonitrile and recorded the thermographic thawing curve. On the basis of these experiments they concluded that ~30% of the polymerisation takes place at -196°C during the irradiation and that the remaining ~70% takes place close to the phase transformation of acrylonitrile in the range from -140° to -100°C during the thawing.

Recently, Tal'roze and Kritskaya [69], in the Institute of Chemical Physics, carried out experiments on the polymerisation of acrylonitrile under slightly different conditions (a thin film of the frozen monomer was irradiated with electrons with an energy of 2 keV, whose path in the substance was much less than the thickness of the film and amounted to only 0.25 μm), using an extremely efficient adiabatic calorimeter. The measurement of the heat liberation was carried out directly under the beam. The experiments which they carried out in 1964 showed that rapid polymerisation takes place at the temperature of the phase transformation (-135°C) whereas, according to the latest data from the experiments which they continued, no reaction takes place at -196°C.

Thus the three groups of authors obtained contradictory results in the study of the polymerisation of acrylonitrile: the first group concluded that polymerisation takes place entirely at -196°C and not at all while thawing; the second group concluded that polymerisation under the beam takes place only partly at -196°C and partly after irradiation during the thaw, at the phase transformation; and the third group consider that the reaction takes place only at the temperature of the phase transformation and does not take place at all at -196°C. Further studies are obviously necessary in order to reach agreement.

Let us first of all consider the question of why irradiation leads to polymerisation in a solid. Irradiation in a solid (as in a liquid or gas) leads to the production of free radicals, electrons, and ions, which naturally may act as the initial centres for the development of chain polymerisation. In a solid, however, all these particles have a very low mobility (the electrons have a low mobility since they may be captured fairly rapidly by suitable traps). This was confirmed by direct experiments in which the monomers were replaced by substances incapable of undergoing polymerisation. The concentrations of free radicals here could be measured directly by the EPR method. It was found that the concentration of free radicals remains unchanged with time, both at -196°C and also with increase in temperature up to the temperature of the corresponding phase transformation, or, in the absence of such a transformation, up to temperatures comparatively close to the melting point. Under these conditions free radicals recombine rapidly and disappear.

Thus as the temperature of the phase transformation is approached, the mobility of the free radicals increases very rapidly. The same is true of electrons. Buben and Nikol'skii [70] in our Institute observed that specimens previously irradiated at -196° emit light at all phase transformations as the temperature is raised but emit almost no light in the intervals between the phase transformations. This takes place so clearly that they put forward this method (radiothermoluminescence) as an extremely effective and simple method for determining the temperatures of all the phase transformations. It is evident that the electrons captured in various types of trap are liberated and recombine with ions at the temperatures of the phase transformations. An interesting feature is that the phase transformation makes the electrons mobile. It is clear that the sudden rearrangement of the atoms at the phase transformation may create conditions favourable for diffusion processes and for processes of electron transfer.

It is therefore natural that the polymerisation of monomers, initiated by free radicals, ions, and electrons formed on irradiation, will take place particularly readily in the regions of a phase transformation.

It is thus difficult to suppose that polymerisation may take place at temperatures below the phase transformations in solid monomers after irradiation. However, polymerisation directly in the beam can in principle occur at any temperature, no matter how low, since the free radicals, ions, and electrons are produced in a "hot state" so that they may bring about initiation of the growth of the polymer chain. Theoretically, therefore, the possibility of polymerisation at extremely low temperatures is not excluded.

Here, however, it is necessary to make allowance for another feature. If the growth of the polymer chain is to take place rapidly with an activation energy $E = 0$, the monomer molecule being attached must be suitably placed, relative to the terminal radical or ion of the growing polymer chain. In phase transformations, when the molecules can move, this orientation may take place readily. At lower temperatures in the solid, the appropriate orientation takes place with difficulty so that the polymerisation appears to be associated with a fairly high activation energy. In each unit stage in the growth of the polymer chain, however, energy amounting to 14–20 kcal mole^{-1} is liberated. This energy is sufficient to ensure mobility of the neighbouring monomer molecule, that is, to orientate it into the required position. Thus in principle, reaction without activation energy is possible no matter how low the temperature.

Finally, one other important feature must be noted. Polymerisation is accompanied by an increase in the density of the substance, since the distance between the carbon atoms in two neighbouring molecules of the monomer C=C C=C C=C is greater that that in the polymer C–C–C–C–C–C–. Thus the polymer chain developing in the monomer is elongated. In the solid state at low temperatures where there are no phase transformations, the contraction of this chain is very difficult. The chain is frozen in the solid monomer. The elongated molecule may thus be thermodynamically unstable. Polymerisation in the beam is then impossible at low temperature.

It is not excluded that for monomer molecules situated along defects, for example, on the surface of fine crystallites, reaction with contraction of the resulting polymer chain may have a fairly high probability, or at least a probability which is immeasurably greater than that in the bulk. This may be the reason for the so-called "limiting" of the yield of polymer under the beam, observed by Kargin and coworkers[71]. "Limiting" of the yield of polymer is observed from liquid nitrogen temperature to the phase transformation temperature, the maximal yield under the beam being measured in percentages of the total concentration of original monomer (gradually increasing with the temperature of irradiation), whereas Barkalov and coworkers[66] have shown that the "limitation" of the polymer yield is removed by irradiation at the temperature of the phase transformation and above, that is, here the polymerisation may take place throughout the entire volume.

Let us now turn to the most important problem of how the chain propagation reaction in the solid phase can take place with zero activation energy.

Polymerisation processes in the liquid phase, which have been fairly well studied, are of two kinds.

1. Radical Polymerisation

Radical polymerisation occurs under the influence of free radicals A$^{\cdot}$, obtained either by irradiation with light of appropriate wavelength or by the spontaneous decomposition of traces of peroxide mixed with the liquid monomer or its solution:

$$A^{\cdot} + C{=}C \rightarrow A{-}C{-}C^{\cdot},$$
$$A{-}C{-}C^{\cdot} + C{=}C \rightarrow A{-}C{-}C{-}C{-}C^{\cdot}, \text{ etc.}$$

For radical polymerisation in the liquid phase the activation energy of chain growth amounts to 3–5 kcal mole^{-1}. There are no grounds for considering that in the solid this energy can be equal to zero. Radical polymerisation therefore cannot explain the temperature dependence of the reaction rate which we observed, if it were to reflect accurately the course of the reaction under the beam. Closer examination of the suggestion that energy is liberated at the moment a chain grows one unit shows that it cannot explain the fact that the activation energy is equal to zero or the production of long purely energetic polymerisation chains.

2. Ionic Polymerisation

This type of polymerisation takes place in particular under the influence of the acids XI. Ionic polymerisation can be represented schematically:

$$I^{+} + C{=}C \rightarrow I{-}C{-}C^{+}, \quad \text{chain initiation}$$
$$I{-}C{-}C^{+} + C{=}C \rightarrow I{-}C{-}C{-}C{-}C^{+}, \quad \text{chain propagation}$$
$$I{-}C{-}C{-}C{-}C^{+} + C{=}C \rightarrow I{-}C{-}C{-}C{-}C{-}C{-}C^{+}, \text{ etc.}$$

Despite the large number of ionic polymerisation processes, the mechanism of ionic polymerisation is insufficiently clear. It is suggested that the $C{-}C^{+}$ ion is accompanied by a counter-ion Z, so that it is correct to represent the terminal group of the growing polymer in the form $I{-}C{-}C{-}C{-}C^{+}\ Z^{-}$ + C=C. When the next monomeric molecule is attached, the positive charge is transferred to the terminal carbon atom of the polymeric radical formed. The counter-ion moves simultaneously to the same carbon atom $I{-}C{-}C{-}C{-}C^{+}\ Z^{-}$.

In a liquid medium this movement is difficult, particularly if the Z^{-} ion is solvated, and this explains the activation energy (~3000 cal mole^{-1}) for ionic polymerisation. Without these complicating features (the presence of the counter-ion, solvate sheaths, etc.), for example, if the polymerisation took place in a vacuum, the actual process of attachment of a monomer with "overflow" of electrons, and hence the movement of the positive charge along the growing carbon chain, would probably take place without any activation energy. Justification for this suggestion may be provided by the experiments of Tal'roze[72] in the Institute of Chemical Physics and of Stevenson[73] in the USA, who observed various reactions of ions with molecules in a vacuum, in the chamber of a mass spectrometer. It was found that for almost all exothermic reactions of this type the activation energy is zero. Moreover, American[74] and Canadian[75] workers have recently shown that in the ion sources of a mass spectrometer at comparatively high pressures, ionic polymerisation reactions take place to give chains consisting of up to 8 units, with an activation energy almost equal to zero. In solutions, however, ionic reactions always require an activation energy because of the presence of solvate sheaths and interaction with the ions of opposite charge. This might explain the existence of activation energy in the liquid phase and its absence in the solid phase.

In a solid, particularly at low temperature, irradiation with fast electrons or γ-rays, in my opinion, produces a situation which is much closer to the conditions of experiments in the chamber of a mass spectrograph than to the conditions of chain growth in the liquid phase. Here, two features are important. The first is the production, in the solid or in the liquid under the influence of ionising radiation, of secondary electrons with an energy of 10–30 V. These electrons move out from the ion to distances which are considerably greater than the radius of the influence of any existing coulombic forces. They are then captured by an impurity or trap of some sort. The difference between the liquid and the solid (without the phase transformation) is that in the liquid (and also in the phase transformation), the mobility of the ion or the electron combined with the trap is sufficient to ensure rapid approach of the ion and electron with the formation of an ion pair. As we have already noted, the electrostatic forces holding this pair together prevent the growth of the ionic polymer chain without activation. In the solid, however, particularly at low temperature, both the ion and the electron captured by the trap are almost immobile, so that here, as in the chamber of the mass spectrograph at low pressures, the ion may bring about growth of the polymer chain without any activation energy.

A second possibility is that a comparatively fast electron with an energy of ~ 10–30 V geometrically does not go anywhere, but enters the semi-conductivity band and with the charge of the ion forms an electron–hole pair, which may exist for a fairly long period in the form of an exciton, moving in the solid with almost no resistance. The moving particle may then bring about rapid polymerisation. The polymer chain will thus be as it were the track of the motion of the exciton, which is naturally retarded by the necessity for movement of the carbon atoms of the polymer chain, corresponding to hundredths of an Ångström unit. In this instance the rate of movement of the exciton, and the rate of growth of the polymer chain, have values of $\sim 10^5$ cm s^{-1}. Chain termination will be determined by disappearance of the exciton.

As we saw above, until recently all experimental data indicated that the polymerisation of a number of monomers takes place completely or for the most part directly under the beam at low temperatures down to -196°C. Recently, workers in our Institute[76], Abkin[77] in the Karpov Physical Chemistry Scientific Research Institute, and Magat in France began experiments to study polymerisation at liquid helium temperatures. It has already been found that after irradiation at the temperature of liquid helium, the monomers after de-freezing give a polymer in yields close to those observed with irradiation in liquid nitrogen. Here also, however, we are still left with the problem of whether the resulting polymer is produced during thawing.

If polymerisation directly at 4.2°K were firmly established, the only explanation would be the possibility of energetic polymerisation chains, and this would require the introduction of essentially new theories into chemical kinetics, for example, the introduction of the exciton hypothesis. This might open a new page in kinetics.

As we have seen, however, new experiments which contradict this suggestion have recently been carried out. They lead to the conclusion that polymerisation of acrylonitrile under the beam does not take place at -196°C. If future confirmatory experiments by all workers show that this is indeed so, at first sight all this will naturally seem much more trivial. The state of a substance in a phase transformation is analogous to the liquid state or to the state of the solid monomer close to the melting point.

If we think carefully, however, the situation here is not so simple either. Thus in the irradiation of acrylonitrile and formaldehyde, on going from the liquid to the solid monomer, that is, at a temperature only just above the freezing point, the reaction rate in the solid state is greater than that in the liquid state by a factor of 25 for the first and by a factor of 100 for the second. It must be remembered that there are also instances, for example, the radiation polymerisation of HMCTS, when almost no reaction takes place in the liquid phase on irradiation, whereas in the region of the freezing point the rate of conversion immediately reaches very high values, gradually decreasing with further decrease in temperature. Many other similar facts could be cited.

Thus the solid state may in many instances facilitate polymerisation. It is often said that in the solid state intermediate polymeric species may be produced in the form of chains of monomer molecules with correct angular orientation relative to one another, close to that corresponding to the disposition of the C atoms in the polymer chain. In other words, we have as it were the formation of characteristic "polymonomeric" complexes, preceding the polymerisation and facilitating its development after initiation, when one of the monomer molecules is ionised. This situation cannot be realised in a readily mobile liquid monomer. As noted by Kargin[78], in the solid state close to the melting point or in a phase transformation where limited mobility is possible, the most favourable conditions are created for optimal mutual arrangement of the molecules and the production of this type of association. This hypothesis also, however, has not yet been confirmed by direct experiment.

Moreover, another important feature must be noted here. Until now no direct measurements have been made of the rate constant for chain growth at the temperatures of phase transformations (in particular close to the melting point). Thus basically we do not know whether chain growth takes place here with or without activation energy. It must be borne in mind that correct arrangement of the monomer molecules does not in itself eliminate the activation energy, which should then be partly the same as that for the liquid phase (since in the liquid phase the molecules "select" the reaction path corresponding to the lowest activation energy). If the activation energy close to the phase transformations and at the melting point is to be lower than that in the liquid phase, or in the limit equal to zero, we require not only correct arrangement of the monomer molecules, but also the formation of appropriate "polymonomeric" complexes. A fairly wide range of phenomena are now known, in which complex formation may facilitate a reaction considerably, not only as a result of an increase in the pre-exponential term, but also as a result of a decrease in the activation energy. It is possible that on appropriate initiation, almost instantaneous transformation of the "polymonomeric complex" into a polymer chain may occur.

In conclusion I would like to describe some quite different experiments which also indicate, however, that extremely rapid polymerisation processes take place even in the absence of any special chemical chain initiators. Dremin in our Institute has developed an extremely interesting method of studying chemical reactions and phase transformations under the influence of shock waves which are excited using explosives and are propagated through

the solid monomer. Pressures varying from 10 000 to hundreds of thousands of atmospheres are produced in the front of the shock wave. It has been found possible to obtain much information on chemical transformations from the form of the shock front. Dremin has recently extended this method considerably by finding a technique for preserving specimens subjected to the action of the shock wave without allowing their breakdown by the action of the wave. In addition to providing the information obtained by studying the shock front passing through the starting material being studied, this has made possible direct observation of the transformations which occur in it.

A number of results have already been obtained by this method and published. Here, however, I shall mention only the polymerisation processes studied by this method by Barkalov, Gol'danskii, Dremin, Tal'roze, Yampol'skii, and their coworkers[79,80]. It was found that extensive polymerisation of many monomers takes place in the solid state under the influence of a shock wave. Study of the form of the front shows that the polymerisation process takes place in the front of the shock wave in a time interval less than 10^{-8} s. The calculated temperature of the monomer in the shock wave does not exceed 200–300°C. We know that almost no polymerisation takes place at these temperatures in the absence of initiators. We may also note that the yield of polymer remained unchanged when the monomer was cooled to liquid nitrogen temperature, so that we are here dealing with a pressure pulse. Thus the chief role in the polymerisation is played by pressure. The curves giving the form of the shock front indicate that this extremely rapid polymerisation takes place when the pressure in the shock front reaches a value at which the density of the monomer becomes close to that of the polymer under ordinary conditions. This is natural, since at this density the distance between the carbon atoms in the C=C C=C monomer becomes almost equal to the distance between two C atoms in the polymer C–C–C–C. Here, however, the movement of electrons from the C=C C=C groups in the monomer into the C–C–C–C groups in the polymer apparently does not require any activation energy when initiation occurs because the shock wave reduces the marked friction in the specimen.

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THE INFLUENCE OF COORDINATION ON THE REACTIVITY OF ORGANOMETALLIC COMPOUNDS

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I. INTRODUCTION

In attempting to answer the question implied in the title, it must first be recognised, as do Dewar and Thompson [1], that estimates of reactivity generally follow two main directions on the basis of: (a) different charge densities, bond orders, polarisability, etc.; or (b) a different in the energies of the reactants and of the transition state. From the standpoint of strict kinetics, only the second approach is legitimate. All constructs which ignore transition states are incorrect in principle. However, the second approach encounters serious theoretical difficulties [1], and in organometallic chemistry only the first has yet been practical, the approach of coarse correlations, giving only an approximate idea of the comparative reactivity of various compounds. The present work is not an exception in this sense.

The various reactivity series for the metal alkyls [2] are widely recognised as too generalised. It is evident that such series cannot be applied to reactions which differ in nature and in mechanism. In speaking about the comparative reactivity of organometallic compounds in a series of different reactions these reactions must be divided into groups similar in some features which play a decisive part. Practice shows that to a first approximation two types of organometallic reaction must be distinguished — additions to multiple bonds and substitutions. Neglect of these simple considerations necessarily leads to confusion both in the comparative evaluation of the reactivity of different compounds, and also in the evaluation of the influence of different complex-forming media on the activity of the same compound. To avoid this widespread error mainly substitutions will be considered.

Furthermore, following the now commonly accepted point of view, it must be assumed that in most such reactions the breaking of the metal–carbon bonds is heterolytic