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## Some problems relating to chain reactions and to the theory of combustion

*Nobel Lecture, December 11, 1956*

I should like to report here on researches into the field of chemical kinetics and the processes of combustion conducted over the last 20-30 years, firstly in my laboratory at the Leningrad Physical-Technical Institute and then in the Institute of Chemical Physics in the Academy of Sciences. These researches represent the outcome of many years' endeavours by a large group of scientific collaborators, many of whom have now become well-known authorities and leaders in individual branches of scientific learning. There can be no doubt that it is indeed thanks to the joint work, thanks to the continual mutual help, and at the same time thanks to the personal initiative of some members of our group that we succeeded in achieving the results which have been valued so highly here.

Successful exchanges of views and friendly discussions with learned men in other countries, particularly with Sir Cyril Hinshelwood, contributed much to the development of these researches and, particularly in the initial stage, to the development of new ideas. From our own experience, we have come to the conclusion that only the joint activity of men of learning in various countries can create conditions under which science can achieve successful further development.

Our investigations can be divided into two different groups, which are however closely linked with each other:

- (1) the application of chemical kinetics to problems relating to the theory of combustion and explosion processes;
- (2) the mechanism of chemical reactions, particularly chain reactions.

Every combustion or explosion process is above all a chemical reaction between the components of the combustible mixture, accompanied by the liberation of heat and various kinds of motion in gases. For this reason, all phenomena which occur in the combustion process are closely linked with the ideas and laws of chemical kinetics, and above all with the velocity of chemical reaction under non-isothermal conditions. According to Arrhenius' law, the heat generated by the reaction itself increases the velocity of

reaction. The existence of such retroaction is to the greatest possible extent characteristic of most phenomena of the combustion process.

As a result of the reciprocal effect of the reaction on the generation of heat in the mixture on the one hand and the increase in reaction velocity due to this greater heat, as already mentioned, on the other, a self-accelerating surge of heat is set up which we term auto-ignition. The dissipation of heat on the walls of the vessel renders the development of a heat surge possible only under certain conditions which are therefore all-important to the temperature of this auto-ignition. This temperature, which is a relative value (and by no means a constant of the substance, as was previously assumed by some authorities), is a function of the kinetic and thermal parameters, namely of the order of reaction, the activation energy, the density and composition of the combustible mixture, the heat of reaction and the dissipation of heat on the vessel walls.

Over the years 1928-1940, we gave<sup>1</sup> a mathematical formulation of the heat theory of auto-ignition, the conclusions of which were subsequently tested on many occasions experimentally, initially in the USSR and then in other countries. If the constants of reaction velocity and conditions of heat dissipation were known, it was possible to calculate beforehand the temperature of auto-ignition (flashpoint) at various pressures. The heat theory made it possible for any reaction of the auto-catalytic type, of which the kinetics were known, to calculate in advance the time of the explosion delay (sometimes as much as several minutes or even hours), as a function of the temperature and pressure.

The theory of normal flame propagation is based on the idea that the burning layer ignites adjacent cold layers due to the dissipation of heat. In earlier theories, it was assumed that the neighbouring layers ignited when the latter were heated to the temperature of auto-ignition, or Aashpoint. However, this disregarded the chemical peculiarities of the process, in fact the chemical kinetics, which was not right and was in itself contradictory. Immediately after the excellent research of B. Lewis and G. von Elbe<sup>2</sup> into flame propagation in ozone (the authors did not indicate the temperature of auto-ignition but did take into account the diffusion of the fresh gas in the flame area), our group succeeded in developing a general heat theory for flame propagation in gases<sup>3</sup>, and also a theory regarding the combustion of liquid and solid secondary explosives<sup>4</sup>. This theory provided a possibility of calculating the normal rate of flame propagation as a function of purely kinetic and thermal parameters. We tested this theory subsequently against

the combustion of carbon monoxide and oxygen mixtures and the combustion of liquid nitroglycol.

Soon after, the theory of the limits of concentration of normal flame propagations, a phenomenon so important to safety techniques, was also forthcoming. We explained this phenomenon by describing how the heat losses on the walls of the pipes in which the flame is propagated reduce the flame temperature and the rate of propagation; the lessening in the propagation rate, however, naturally leads to an increase in the heat losses. Considering this retroaction mathematically, it follows that the rate of propagation cannot be less than a certain value, which explains the existence of concentration limits in the propagation of flames.

The part played by mechanical motion, particularly turbulence in the gas, during flame propagation has long been noted. It was demonstrated however with particular clarity in our institute<sup>6</sup>. For example, it was shown that, if a wire spiral is applied along the inner wall of a glass tube containing a mixture of carbon monoxide and air, the rate of flame propagation in this mixture is approximately one thousand times greater than it is in the same glass tube but without the spiral of wire. The theory of turbulent combustion developed by G. Damköhler<sup>7</sup> and by the colleagues in our institutes is based on the idea that the surface of the flame front increases by virtue of pulsations. The overall flame propagation rate is determined in such cases largely by the square root of the quadratic mean of the pulsation rate, which means that it increases with increasing turbulence.

If the flame is propagated in tubes of sufficient length, it is accelerated due to turbulence in the fresh mixture. This acceleration of the flame produces a detonation condition in the combustion, ignition occurring due to the high temperatures generated due to compression of the gas in the percussion wave. In large diameter tubes, the detonation rate in mixtures bordering on the stoichiometric and having adequate reaction heat, does not depend upon the kinetics of the reaction, in accordance with the traditional theory of detonation, which allows of instantaneous combustion of the substance in the surge front. This theory cannot however explain why low-energy mixtures (diluted particularly by inert gases or mixtures at low pressure) do not detonate at all, why there are limits to concentration of detonation, why high-energy mixtures do not detonate in narrow tubes, etc. The dependence of the capacity for detonation upon chemical kinetics was demonstrated with particular clarity in our institute, taking a mixture of CO and air as the examples. The velocity of reaction between CO and air is known to increase

markedly in the presence of traces of hydrogen. It proved that mixtures of CO and air do not detonate but that the introduction of 1% hydrogen into such mixtures renders them capable of detonating.

A theory of detonation was developed in the institute which took reaction kinetics (i.e. the width of the reaction zone) into account<sup>10</sup>. In this theory, all the questions mentioned relating to detonation capacity and its limits found a semi-quantitative explanation, similar to the explanation of normal flame propagation limits.

A noteworthy phenomenon, the so-called "spin detonation" discovered by C. Campbell and W. A. Bone<sup>11</sup>, was tested exhaustively in our institute<sup>12</sup>; these experiments led to the development of the first theory of this remarkable process.

We see now how comprehensive investigation of the chemical, physical, and mechanical peculiarities of a phenomenon and their reciprocal effects by a relatively small group of scientific collaborators in the Institute for Chemical Physics (A. V. Sagulin, O. M. Todes, D. A. Frank-Kamenetskii, Yu.B. Chariton, A. Ya. Apin, Ya. B. Zel'dovich, A. F. Belyaev, P. F. Pokhil, K. I. Shchelkin, A. S. Sokolik, O. I. Leipunskii) in conjunction with some foreign authorities (C. N. Hinshelwood, A. C. Egerton, B. Lewis, G. von Elbe, W. Jest, G. Damköhler, P. F. Laflitte, F. P. Bowden, T. von Kármán and many others) made it possible to lay the foundation of today's theory of combustion and explosion processes in gases and explosives.

There are virtually many respects in which this theory is not completely clear, and a vast field of work still confronts us all, but the main paths towards resolution of the problem are already marked.

In the years 1926-1927, we came in contact with another direction which constitutes a basic direction in chemical kinetics and which illustrates the intimate mechanism of chemical reactions. We established that not every auto-ignition is thermal in nature, but that there is a second, quite different kind of auto-ignition which we termed chain-ignition.

Thirty years have passed since Yu. B. Chariton and Z. Valta's discovered the lower limit of phosphorous ignition and since I concerned myself<sup>14</sup> (to a certain extent in conjunction with A. I. Shal'nikov) with research into the properties of this phenomenon, as well as since the first experiments at explaining this phenomenon theoretically by notions of branched chain reactions and their termination at the vessel walls (soon afterwards, this was proved in direct experiments by A. Trifonov<sup>15</sup>). The results obtained were so significant that the investigation of chain reactions, particularly

branched chain reactions, became the principal problem of the Institute for Chemical Physics for many years.

The branched chain surge can occur under isothermal conditions (in which the heat of reaction is fully dissipated), whereas in the thermal surge, the dissipation of the heat renders an explosion impossible. In the branched chain reaction, active particles, namely free radicals, are produced, the number of which grows quickly, due to the branching of the chain.

It is therefore enough for one single free radical to be produced (for example thermally) for the radicals to multiply, which leads to a rapid reaction of the chain ignition type.

The theory was examined particularly thoroughly in the experiments conducted by V. N. Kondrat'ev, E. I. Kondrat'eva<sup>16</sup> and L. I. Avramenko<sup>17</sup> who investigated the reaction of chain ignition in hydrogen-oxygen mixtures (close to the limit where the temperature of the flame does not exceed 700 to 800°C), and in the experiments of N. M. Emanuel<sup>18</sup>, who was concerned with the slow reaction of hydrogen sulfide oxidation (the reaction took some minutes). In both cases, the presence of radicals (H, OH, SO) was observed directly, the number of H atoms rising up by 10% compared with the starting hydrogen, under certain conditions and during the oxidation of the hydrogen, whilst the number of SO radicals rose, during oxidation of the hydrogen sulphide by up to 40% as compared with the outset. At the end of the reaction, naturally, all the radicals had disappeared. The radicals disappear because they are trapped by the vessel walls, because they react with special admixtures or by virtue of recombination processes. This is when the chains break.

Where branched chain reactions are concerned, there are two possibilities: (1) the rate of branching exceeds that of termination, which results in very rapid development of the chain avalanche; (2) the rate of termination is greater than that of branching, so that the avalanche cannot develop and the reaction cannot even take place (if, as is usual, the rate of free radical formation is quite low); then, for example, phosphorous vapours may stay below the limit for days and in contact with oxygen without even a trace of reaction processes being observed. The transition from a completely inert state to a violent reaction (explosion) can easily be caused by for example increasing the pressure of the oxygen or the dimensions of the vessel, or by inserting tiny metal wires which violently absorb the free radicals, into the vessel or withdrawing such wires from the vessel, or by adding inert substances, etc. The transition from a practically entirely inert state to an en-

ergetic reaction occurs if one of these parameters varies within extremely close limits which, on some occasions, are virtually unmeasurable. Similar limit phenomena were observed by Sir Cyril Hinshelwood and collaborators<sup>19</sup> in the case of pressures which exceed a certain "second upper limit" (e.g. in the case of the reaction of water formation from oxygen and hydrogen). The second upper limit was explained on a basis of the ideas put forward by Sir Cyril Hinshelwood regarding chain termination in the volume in the case of threefold collisions and the concept of chain branching.

This meant that both our investigations and those conducted by Sir Cyril Hinshelwood<sup>19</sup> and his collaborators led to the establishment of a new idea of the reaction limit, as the result of each branched process which is accompanied by chain termination. These researches were conducted at the end of the twenties and start of the thirties.

When, at the end of the thirties, the physicists discovered branched nuclear reactions, similar limit phenomena were observed as with the chemical reactions, in spite of the difference which obtained in principle, because limit phenomena of this type characterize any branched chain reaction. With nuclear reactions, it is possible to observe with particular clarity the transition from the perfectly inert condition to an accelerated reaction or even explosion, following a change in such parameters as size and density, etc. (for example when control rods are introduced into or moved out of nuclear reactors).

From the field of the slow chemical reactions, we ought first to quote chain reactions with degenerate branching. These reactions are characterized in that their primary product is a molecular intermediate which enters relatively slowly into the reaction leading to the formation of free radicals. The existence of such reactions was proved even in the thirties, when it was established that the reactions of hydrocarbon oxidation are degenerately branched. The theory of "degenerate explosions", which we developed in 1931-1934<sup>20</sup> is today generally accepted.

As is shown by the work of A. Ya. Apin<sup>21</sup>, not only the oxidation processes but also the decomposition of nitrogen chloride has the character of a branched chain reaction with an upper ignition limit.

Most other chemical gas reactions constitute unbranched chain reactions. With such reactions and also with the branched reactions, chain propagation takes place rapidly due to the formation of free radicals. Since however there are no branchings, there is no spontaneous development. Each chain is produced only by reason of the action of a spontaneously forming free

radical (e.g. under the dissociation of the starting substance due to thermal motion).

At this point, I would like to review the development of notions in the field of chemical processes. The problem of chemical transformations and the regularity observed thereby is probably one of the main problems of chemistry and chemical technology. That is why the development of the general theory of chemical reactions and reaction mechanisms is so important.

Actually, the significance of this question was acknowledged by chemists (particularly by those who were active in the field of organic chemistry) some considerable time ago, and they systematized their years of experience in the form of various reactivity rules which were often connected with the theory of structure. Unfortunately, these rules were in most cases only qualitative; they had many exceptions and were often dependent upon the test conditions. Nowadays, roughly a hundred years since the advent of the theory of structure, questions of reaction velocity are dealt with from an electronic and quantum-mechanical standpoint. There can be no doubt that great progress has been achieved in this field. Nonetheless, the theory still remains qualitative and often we have to make do by just substituting one certain terminology for another.

In the second half and particularly in the last quarter of the last century, chemists' attention was drawn to another aspect of chemical reactions which I should like to characterize as physical. From that time on, physical chemistry became acknowledged as an independent science which introduced thermodynamic and statistical methods of investigation into chemistry. And so chemical kinetics—the science of the velocity of chemical reactions—was created. The first successes in this field and in other fields of physical chemistry are linked with the names of J.H. van 't Hoff and S. Arrhenius.

Van 't Hoff and Arrhenius discovered some basic laws of chemical kinetics. In the view of Van 't Hoff, all chemical reactions ought to occur as simple mono- or bimolecular reactions if only their progress is not affected by perturbation influences; these latter might for example be caused by secondary reactions, the liberation of heat or catalytic effects.

With the exception of Van 't Hoff himself, who was greatly interested in perturbation influences of this type, most authorities confined themselves in the decades which followed to investigating the kinetics of such reactions as followed the simple laws. Since the number of such reactions is quite small, this limitation led to inhibited development of kinetics.

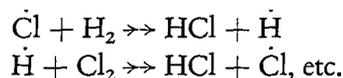
Nonetheless, it must at this point be remarked that, at the end of the last

and the beginning of the present centuries, a number of investigators were concerned also with complicated reactions in the field of conjugated oxidation, homogeneous catalysis and auto-catalysis in electrolytic solutions. I am referring to the work of Wi. Ostwald, N. A. Menshutkin, D. P. Konovalov, R. Luther, F. Haber, A.N. Bach, S.Engler, N. A. Shilov, V. Goldschmidt, J. N. Brønsted and others. Among these workers, there were many which drew attention to the significance of often unstable intermediates to the course of chemical reaction.

It was roughly about this time that Max Bodenstein started his scientific activities. In his investigations in the field of gas reactions, he concerned himself not so much with tracing simple reactions but was on the contrary interested in the course of complicated reactions (see for example his classic work on the reactions between hydrogen and bromine, 1907). As is well known, Bodenstein, in investigating photochemical reactions of chlorine and hydrogen, made in 1913 the outstanding discovery of the enormous quantum yield of this reaction which contradicted Einstein's law.

And so the idea of chain reactions was introduced into chemistry for the first time\*. It is impossible to overestimate the importance of this work to the development of chemical kinetics as a whole.

A correct interpretation of the mechanism of the hydrogen-chlorine reaction was given some years later by W. Nernst, who assumed that the chlorine molecule decomposed under the action of light into two atoms which initiated a long chain of transformations:



Enlarging on the findings of M. Bodenstein, J. A. Christiansen, in 1924, connected the inhibiting action caused by traces of a few active additives (inhibitors) on oxidation reactions in liquids, with the chain-nature of the reaction process and with the termination of the chain produced by these inhibitors.

In 1927, Bäckström proved the accuracy of this supposition and used this method to establish the chain mechanism of various reactions. For some reason, no adequate importance was attributed to this work. In reality, it is among the most important works in the history of chain reaction.

• A review of the history of the development of chain reactions up to 1934 is given in the book *Die Kettenreaktionen* (Chain reactions) by N. N. Semenov<sup>20</sup>.

I would also like to mention the work of J. A. Christiansen and Kramers in 1923, when they applied the chain theory to thermal reactions, particularly monomolecular reactions. The truly interesting view formulated by these authors relating to pure energy chains could not subsequently be confirmed by experiment, so it was dropped. Nevertheless, it is possible that in individual radical reactions, energy factors play an important role; this is demonstrated particularly by the interpretation of the positive interaction of chains which we observed and by considerations of fast reactions in hot flames, as described recently in the literature<sup>22</sup>.

And so we see that increasing interest was devoted to chain reactions in the twenties. Certainly, at that time, the number of chain reactions known was fairly small and such reactions seemed rather to constitute an exception.

In the years 1926-1928, both C.N.Hinshelwood<sup>19</sup> and we commenced investigations in the field of chain reactions. In 1934, in my book *Chain Reactions*<sup>20</sup>, I had the following to say regarding the importance of these works:

"In 1927-1928, in Oxford, Leningrad and to a certain extent in Princeton, the chain theory was applied to investigate the reaction of such substances as are capable of igniting and exploding.

The most important feature resides in the fact that the theory was very closely linked with experiments which led to the discovery of new phenomena and also to the explanation of some long-known but hitherto incomprehensible phenomena. These works made it possible to draw up quantitative laws for chain reactions valid for a large group of phenomena and simultaneously made it possible to define the specific field of these phenomena. As the result of such works, increased interest was given to reactions of this kind, which, in 1930-1933, led to many new investigations being conducted. We would like to think that these works constitute the basis for a redevelopment of chemical kinetics."

In the years 1929--1935, a large number of the most widely diverse experiments were conducted to explain and further develop the theory. Apart from our group of collaborators (V. N. Kondrat'ev, A.V. Sagulin, A. A. Koval'skii, Yu. N. Ryabinin, A.Trifonov, M.B.Neuman, V.R.Bursian and V. S. Sorokin, A. B. Nalbandyan, N. M. Chirkov, F. I. Dubovitskii) and the Hinshelwood group (H. W. Thompson, C. H. Gibson) various other researchers, e.g. .B. H. L. Emeleus, R. G. W. Norrish, H. W. Melville, E. B. Ludlam, R. N. Pease, B. Lewis, G. von Elbe and many others concerned themselves with branched chain reactions.

The year 1931 saw the publication of works by F. Haber and R. Willstätter in which it was shown that ions of varying valence can readily form free radicals in some solutions. In the view of these authors, some important organic, particularly biochemical, reactions follow a chain mechanism.

In 1934, my book *Chemical Kinetics and Chain Reactions* appeared in which a general theory of branched and non-branched chain reactions was presented and in which it was shown, on the basis of experimental data, that such reactions formed by far the biggest part of gas reactions and are often to be encountered in chemical transformations in the liquid phase.

The accuracy of the supposition that polymerization processes also have a radical-chain nature was proved shortly afterwards experimentally by, among others, S. S. Medvedevas; F. O. Rice (USA)<sup>24</sup> and, later on, A.V. Frost (USSR)<sup>25</sup> proved the chain mechanism of cracking processes.

A substantial difference between the traditional theory of chemical reactions and the chain theory resides in the fact that the latter is not delimited by any perturbation influences but, on the contrary, sets out to provide general theoretical bases, with consideration to the courses of these influences. The laws of Van 't Hoff and Arrhenius still form the foundation of chemical kinetics but, in the majority of cases, they ought only to be used for elementary reactions.

The importance of chain reactions to technology is shown by the fact that most industrial processes, such as for example cracking, combustion, polymerization, slow oxidation, chlorination, are all typical chain reactions. The field of chain reactions and radical reactions has become a principal branch of modern theoretical chemistry.

At present, various laboratories both here and abroad (in this respect, I would like particularly to mention the successful work of the School of E. W. R. Steacie) , are exhaustively investigating the mechanism of chain reactions; methods are being developed to form and examine free radicals. Moreover, the effect of the structure of the radicals on their chemical activity and various other questions appertaining thereto are being investigated.

I should now like to report rather more about the work of our institute which has interested me particularly during the last 5-6 years. Some of the work was commenced only a short while ago; I would therefore like to stress that some of the theoretical conclusions cannot as yet be regarded as final.

Of great interest is the problem of competition of chain reactions and ordinary molecular reactions which are not accompanied by the formation

of radicals. Chain propagation (a reaction between molecules and radicals) usually occur at a fairly high velocity, at least where the temperature is relatively high. The slowest stage is the initiation of a chain which is often combined with increased activation energy. For this reason, the reaction rate is in fact higher with artificial chain initiation (e.g. in the case of photochemical processes or by the action of additives) than for any molecular reaction. If no such artificial chain initiation occurs, then considerable significance must be attributed to the formation of free radicals by molecules participating in the reaction. The easiest way to form free radicals lies in the decomposition of the weakest bond of the molecule. The extensive investigations into elementary decomposition reaction carried out recently by M. Szwarc<sup>26</sup> and other authors (to a certain extent in our institute also) showed that, in some cases, the decomposition of molecules occurs more readily in radicals than in saturated fresh molecules. It follows from this that thermal decomposition of such substances proceeds by a radical-chain mechanism.

In other cases, though, the dissociation into radicals occurs more slowly than into molecules. An example of this is the decomposition of some organic chlorine and bromine derivatives of hydrocarbons. The competition between these two kinds of molecular decomposition depends upon their structure ( $C_3H_5Br$ <sup>27</sup> and  $C_3H_5Cl$ <sup>28</sup> for example split off one halogen atom primarily when they dissociate, whereas  $C_2H_5Br$ <sup>29</sup> and  $C_2H_5Cl$ <sup>30</sup> immediately split off hydrogen halide whilst simultaneously forming olefins;  $CH_3Br$  splits off one bromine atom<sup>31</sup> and, for chloroform, we proved immediate dissociation into hydrogen chloride and the biradical  $CCl_2$ <sup>32</sup>).

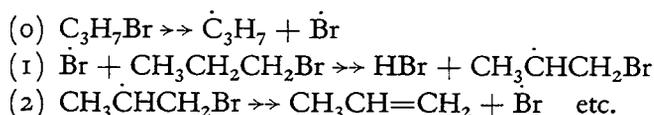
I would like to remark that, in some cases, even at a somewhat higher rate of decomposition into molecules, chain reaction can be decisive. This can be explained in that, due to the chain length, the chain reaction can occur more quickly than molecular reaction, even at a low rate of chain initiation.

The question of competition between a molecular and a chain mechanism has been the subject of several discussions, but it cannot yet be regarded as explained. This is partly due to the fact that chain reactions often follow simple kinetic laws and can therefore be similar to molecular reactions. Now, we also know of some reactions for which, under certain conditions, the molecular mechanism can be regarded as having been proved. This is particularly the case when the propagation of the chain is inhibited on account of the molecular structure.

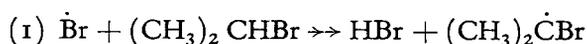
Some interesting conclusions can be drawn from investigations into the

relationship between molecular structure and the mechanism of decomposition which were carried out in our institute and also independently by A. Maccoll<sup>33</sup> and others. For example, the decomposition of two bromides, namely *n*-propyl bromide and isopropyl bromide may be mentioned,<sup>34</sup>. Whilst the first decomposes according to a chain arrangement, the second breaks down directly into molecules of hydrogen bromide and propylene. This can be explained as follows<sup>35</sup>:

in the case of *n*-propyl bromide, the following chain reaction occurs:



whilst, in the case of isopropyl bromide, the reaction



leads to formation of the radical  $(\text{CH}_3)_2\dot{\text{C}}\text{Br}$ , which cannot decompose further, and so inhibits the chain reaction.

Why are chain reactions so widespread?

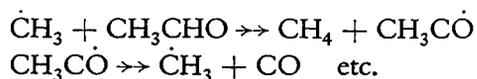
It must be assumed that they are determined by some general fundamental chemical laws.

Firstly, the free radicals are chemically highly active particles and therefore react far more readily with molecules than molecules react to one another (in homolytic reactions).

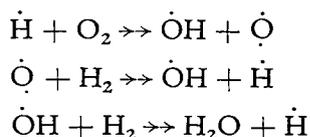
Secondly, the free valence cannot disappear in the course of the reaction between a free radical and a molecule, which means that at least one product of reaction has the character of a free radical. This radical, for its part, again reacts with the nearest molecule, so that another free radical is formed, and in this way, a long chain of changes can take place.

In this respect, three cases are possible:

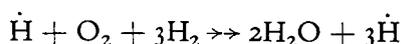
(1) During the course of the reaction between radical and molecule, a monoradical forms, which leads to the formation of an unbranched chain, e.g.



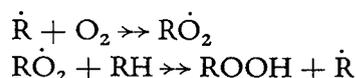
(2) During the course of the reaction, instead of one free valence, three are formed, in other words three monoradicals of which each one in turn starts a chain. The result is the formation of a branched chain reaction, e.g.



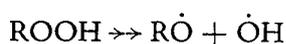
which corresponds to the following overall process



(3) If the main chain of the reaction is unbranched but if, due to monomolecular breakdown of reaction products or if, in any other way free radicals and, consequently, new chains can form, then the characteristic features of branched chain reactions can be discerned in the reaction (auto-acceleration, limiting phenomena). In this case, it is usual to speak of degenerate branchings. As an example, we might quote the formation of alkyl hydroperoxides:

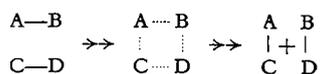


Due to the small amount of decomposition energy in the bond O-O (30 to 40 kcal), the hydroperoxides decompose relatively easily and at the same time form free radicals:



which raises the chain number.

The high reaction capacity of free radicals is first and foremost an experimental fact and can to a certain extent also be explained by quantum mechanics. A calculation along these lines shows that, for the reaction  $\text{A} + \text{BD} \rightarrow \text{AB} + \text{D}$ , namely in a linear arrangement of the atoms in the transitionalstate  $\text{A}\dots\text{B}\dots\text{D}$ . . ., the activation energy is usually not high (not more than 10 kcal). Where two molecules are acting

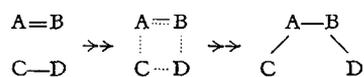


a rectangular transition complex is formed. The molecules CD draw close to the molecules AB in the direction perpendicular to the bond AB; in consequence, the activation energy levels here are high. If on the other hand, in the transitional state, the molecules assume a linear arrangement



then, in the course of the reaction, two free atoms form and the reaction itself is markedly endothermic. Although, as we have been shown<sup>35</sup>, the activation barrier is similarly low, as with the reaction between radical and molecule, the overall activation energy achieves quite high values due to the endothermic process.

With regard to the action of one atom or radical on a n-bond, an approach under a certain angle to the double bond ought probably to be the most advantageous. This activation stage of such reactions is similarly quite low (2-5skcal). A fairly high activation energy in the case of a saturated molecule being added to a double bond



is probably connected with a necessary consumption of energy in the case of changes in configuration of the transition complex. In the case of an atom or radical being added, the configuration changes in the transition state are minimal, which explains the lowness of the activation barrier.

It must be mentioned that the magnitudes of activation energy determined experimentally for reactions between free radicals and molecules are quite various and fluctuate over a fairly wide range from 0 to 14 kcal. M. Polanyi showed<sup>36</sup> that, in a series of reactions between radicals and molecules of a uniform type, when the heat effect  $2$  rose, the activation energy  $\epsilon_0$  diminished steadily, rather following the law  $\epsilon_0 = A - \alpha q$ . Once we had summarized most of the experimental data mentioned in the literature, we were able to show<sup>35</sup> that  $A$  and  $\alpha$ , although they are not the same for different classes, are not greatly different. The empirical relationship  $\epsilon_0 = 11.5 - 0.25q$  gives for  $\epsilon_0$  values which do not differ by more than  $\pm 2$  kcal from values determined by experiment. At present, there are but few exceptions to this rule, mainly reactions with halogen, particularly with iodine.

With an approach of this kind, the activation barrier of the reaction and in consequence also the activity of the radicals and molecules can be deter-

mined as a difference in energy between the molecule bonds which are decomposing and those which are forming. A review of the experimental data for bond energy levels and for reaction capacities of radicals and molecules enables us to conclude that the activity of free radicals varies within fairly wide limits, even in the case of the free valence being linked with one and the same atom (for example C). This is due to the fact that, in the free radical, the p-electron is not paired, which naturally facilitates its interaction with the other part of the radical and leads to considerable conjugation energies in the radical. These energies depend naturally upon the structure of the radical. After the formation of a molecule during the course of the reaction, the electron is shown to be paired; it loses its "mobility" and is then only weakly joined with the other part of the molecule. Particularly marked is the conjugation of the free electron in the free radical in the case of its reaction with p-electrons of conjugated systems of  $\pi$ -compounds of the radical, which reduces the activity of such radicals. But even without such an interaction, substantiatedly easier action is possible through other causes (e.g. changes in configuration).

The facts mentioned make it possible to introduce the concept of relative activity of radicals which is not dependent upon which reaction of these radicals we use to determine them\*. The activity of the radical NO, is 30 kcal less, of the allyl radical 21.5 kcal less, of the benzyl and  $\text{CBr}_3$  radicals 17 kcal less and of the  $\text{C}_3\text{H}_7$  radical 3 kcal less than that of the  $\text{CH}_3$ -radical (in other words the bonding energy R-X is less than for  $\text{CH}_3\text{-X}$  by the amounts shown).

Such approach relationships make it possible to estimate, for not too low temperatures, the rate constants for reactions between free radicals and molecules. This enables us to calculate (though highly approximate) the magnitude of velocity of elementary stages in complicated reactions, such as for example oxidation and cracking. Unfortunately, there is not as yet any clarity as to the steric factor in exchange reactions. According to E. Steacie<sup>37</sup>, the steric factors for many reactions are supposed to be several magnitudes less than one. On the other hand, there are no theoretical considerations which allow us to estimate the magnitude of this coefficient; there are little experimental data available relative to steric factors and what there is, is in most cases contradictory..

\* If we for example assume the activity of the radical  $\dot{\text{C}}\text{H}_3$  to be nil, then the activity of the radical R is determined as a negative heat effect of the reaction  $\dot{\text{R}} + \dot{\text{C}}\text{H}_3\text{X} \rightarrow \text{RX} + \text{CH}_3$ ,  $-q$ . As we have succeeded in showing, the heat effect, in line with the above-mentioned considerations, is almost independent of the nature of X.

Furthermore, there is still little information available about bond dissociation energies, required to determine  $q$ , which, among other things, is tied up with the limited possibilities of the methods used for determining the bonding energy; this also relates to the electron collision method. It is interesting to mention a new method of estimating the bonding energy and proton affinity of the molecule, which has been proposed in our institute by V. L. Tal'roze. This method is based on the fact established by Tal'roze<sup>38</sup> and then by D.P. Stevenson<sup>58</sup> that the activation energy of the elementary reactions of ions and molecules is very small.

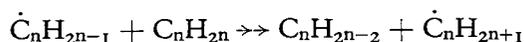
From the field of complicated reactions, we have in recent times been devoting the greatest attention to the slow oxidation processes. It is particularly characteristic of this work that the kinetics of the accumulation of all the main products of reaction should be undergoing investigation and balance be established in the course of reaction. In the gas phase, the thermal oxidation of propylene and propane has been thoroughly investigated. A.B. Nalbandyan<sup>39</sup> investigated the photochemical oxidation of propane and methane. The results gained by V.Ya. Shtern<sup>40</sup> on the kinetics of propane and propylene oxidation make it possible to suggest a reaction mechanism which, in turn, makes it possible to describe the kinetics of the accumulation of most products of oxidation and by-products of cracking. This reaction mechanism is based on the assumption of two competing transformation possibilities of the radical  $RO_2$  which forms as an intermediate product - a bimolecular transformation with hydrogen splitting off from the hydrocarbon molecule and the formation of hydroperoxide and a monomolecular transformation with isomerization of  $RO_2$ , subsequent decomposition of the carbon skeleton and formation of carbonyl compounds (without peroxide forming). The degenerate branching is, from experimental data, probably the result of an oxidation of acetaldehyde.

In the liquid phase, N. M. Emanuel<sup>41</sup> exhaustively investigated the oxidation of cyclohexane and *n*-decane, determining the sequence of the formation of stable reaction products and, probably for the first time, he showed for paraffins and cycloparaffins that all products of reaction form due to the transformation of a primary intermediate material - hydroperoxide. It is interesting to note that the phenomena are somewhat different if the reaction is carried out in a metal apparatus. According to provisional results regarding oxidation of cyclohexane in a steel apparatus, the intermediate stage, with the formation of hydroperoxide, is avoided during formation of the main mass of reaction products. Since, as we know, the alkyl peroxide formation

is a homogeneous chain reaction, such a change in the mechanism shows that the walls of the reaction vessel influence propagation of the chain.

Of great importance to the work was the kinetic method developed by M. B. Neuman<sup>42</sup> using active isotopes; this method made it possible to measure the rate of formation and disappearance of stable intermediates and hence to determine the sequence in which they are formed.

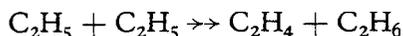
During the course of recent years, our institute commenced investigations into the mechanics of the thermal decomposition of hydrocarbons. Comprehensive attention to literature data regarding cracking processes of olefins led V. V. Voevodskii<sup>43</sup> to conclude that these processes obviously did not, as was hitherto assumed, constitute radical but rather more chain reactions. The mechanism developed by the author is based on the assumption of a hydrogen exchange between free radicals and olefin molecules, e.g. for a radical obtained from olefin  $C_nH_{2n}$



On a basis of this assumption, the author was able to show the composition of the cracking products for a number of olefins.

Of the utmost practical interest is the initiation of a chain, i.e. to the formation of primary free radicals and atoms. To this end, the effect of light, electrical discharge, addition of substances which decompose easily in radicals and, particularly of late, radiation has been used. I would like here to deal mainly with such chain initiation processes as are, in theory, still not adequately clear although they are directly linked with questions of chemical kinetics.

It can be assumed that free radicals often form under the action of two molecules<sup>35</sup> (and not during dissociation of molecules into radicals). As already mentioned, quantum-mechanical calculations show that such reactions can take place with a favourable molecular arrangement yet even without any great activation barrier. This conclusion can also be proved experimentally. It is known that the reaction of two radicals is not by any means restricted always to valence saturation, with a molecule being formed from both particles. It is quite often the case that disproportionation processes occur, as for example



As can be proved by experiment, such reactions exhibit no activation energy

at all, or if they do, then only a very slight one. From this, taking general thermodynamic considerations into account, it follows that the activation energy of the reciprocal reaction of the formation of free radicals, where two molecules are involved, e.g.  $C_2H_4 + C_4H_6$ , must be equal to the heat effect of this process. In this case, the energy consumption is fairly high (62 kcal), yet not as high as in the case of the formation of radicals upon dissociation  $C_2H_6 \rightarrow 2CH_3$  (83 kcal) or even in the case of the dissociation  $C_2H_6 \rightarrow C_2H_5 + H$  (98 kcal).

The chain oxidation of liquid substances is often characterized by a fairly high initial velocity, i.e. by a high rate of initiation. If the above considerations are extended also to such systems, then the reaction must be described in the following way:  $RH + O_2 \rightarrow R + HO, -q$ . If RH is aldehyde, e.g. acetaldehyde, the bonding energy is no more than 80 kcal. The energy of the reaction  $H + O_2 \rightarrow HO$ , was determined fairly accurately and amounts to 45-47 kcal. The heat effect  $q$  is therefore some 35 kcal and is about the same magnitude as the decomposition energy of peroxides. The results established in recent years as regards oxidation of gaseous acetaldehyde and ethyl linoleate have shown that the chain initiation is probably decided by the bimolecular reaction of the oxidizing substance with oxygen. We know too that the addition of oxygen accelerates cracking processes and other organic reactions (e.g. hydrobromation of olefins). In all these cases, the action of the oxygen can be explained by the aforesaid chain initiation:  $RH + O_2 \rightarrow R + HO$ . The energy consumed in this reaction is about 30 kcal, which means that it is of the same magnitude as in the decomposition of peroxides (the bonding energy C-H in the  $CH_3$  group of propylene is 77 kcal).

Many hydrocarbon oxidation processes have the nature of chain reactions with degenerate branchings, which often leads to considerable induction periods. In the liquid phase (e.g. in the oxidation of paraffin), such induction periods often extend to some hundreds of hours. As we know the introduction of small quantities of nitrogen oxides reduces in the gas phase the induction period of oxidation of hydrocarbons at high temperatures; the cause lies in the accelerated formation of radicals by the effect of nitrogen oxides on the hydrocarbon molecule. N. M. Emanuel and his collaborators<sup>44</sup> recently showed that nitrogen oxides have a similar action also during oxidation in the liquid phase, at a relatively low temperature. In order to commence the reaction, it is sufficient to pass air with a low NO<sub>x</sub> content through liquid paraffin for a short time. After such a reaction has been started, continuance of the reaction is ensured by the peroxides which form. At this stage, pure

air can be passed through the paraffin; admixture of nitrogen oxide has even a rather inhibiting effect on the rate of reaction (probably due to decomposition of the peroxides). These phenomena have been proved for both liquid and liquefied paraffins.

According to observations by A. V. Topchiev<sup>45</sup>, methane can be nitrated and chlorinated easily under the simultaneous action of NO, and Cl<sub>2</sub>; chlorination without NO, or nitration without Cl, takes place far more slowly. This can probably be explained by the formation of NOCl which for its part generates chlorine atoms.

A noteworthy phenomenon of chain initiation was discovered recently by N.M. Emanuel<sup>46</sup> in his work on the oxidation of propane in acetone at 180 to 200°C in the presence of HBr. He established that, in the initial state of propane oxidation, a reaction takes place during the few seconds following introduction of the reaction components, during the course of which only infinitesimal quantities of propane are consumed. But actually during the course of this reaction, such active particles form as determine the main stage of the process, which may extend over several minutes. It is interesting to note that the reaction product acetone inhibits the reaction and that, if there is an adequate initial concentration of acetone, the reaction does not take place at all. If, on the other hand, acetone is introduced into the reaction zone after completion of the first stage (fractions of minutes after its commencement), this no longer has any effect at all on the course of the reaction. We see, therefore, that acetone acts only on the first, initiating stage of the reaction. It has not yet been possible to ascertain the chemical mechanism of this process. Possibly it may be a branched chain reaction between HBr, propane and oxygen, during the course of which active intermediates are formed which, in turn, decompose to form free radicals, so initiating the chain reaction of the main stage of propane oxidation.

Although as yet without foundation, the possibility of chain initiation by the solid walls of the vessels opens up vast perspectives.

As a result of the work of A. A. Koval'skii<sup>47</sup> (who worked out a method of differential calorimetry), it may be considered as firmly established that for some heterogeneous catalysts - e.g. bauxite catalysts in the industrial recovery of sulphur from CO and SO<sub>2</sub> - the effect is confined to the initiation of volume reactions on the surface, whereas the actual reaction occurs in up to 96% in the gas phase. Using differential calorimetry, A.M. Markevich<sup>48</sup> demonstrated, some years ago, that the chains of the dark reaction  $\text{H}_2 + \text{Cl}_2$  start on the surface of the glass. A.M. Chaikin<sup>49</sup> came to a similar conclu-

sion for the dark reaction of dichloroethane formation during the chlorination of ethylene. The same author furthermore showed, for the first time and with complete clarity, that the direct addition of chlorine to ethylene does not occur in the gas phase and that the reaction always is of a chain nature, chlorine atoms participating.

As already mentioned earlier, we succeeded in the twenties in proving the possibility of chain termination on solid surfaces. Subsequent research into this phenomenon, both in our country and abroad, showed that atoms and free radicals are almost always chemisorbed by solid surfaces. The activation energy of the chemisorption process depends upon the nature of the surface but it is always fairly low (less than 10 kcal).

Passing on to the theory of reaction initiation by the vessel walls, I would like first of all to establish that the fact of free radicals being trapped by the walls, as has been unequivocally established for the majority of chain reactions, leads, on thermodynamic grounds, to the reverse reaction of radical formation also taking place at the walls.

The initiation of chain reactions by the vessel walls has also been established in the decomposition of alkyl chlorides. Even earlier, it was known that, in clean, untreated vessels, this reaction takes place considerably more quickly (some magnitudes more quickly) than in vessels the walls of which have become coated during the course of repeated reaction processes. This phenomenon cannot be explained as heterogeneous catalysis on clean surfaces. Tests carried out recently in our institute with varying proportions of surface to volume, and also tests using differential calorimetry, show fairly clearly that, in many cases, the reaction is virtually homogeneous both in clean as well as in treated vessels. These facts can only be explained by assuming that the chain reaction is initiated on the surface. Obviously, this process takes place easily on clean surfaces and is made markedly more difficult on treated surfaces. Some researchers (Barton, Howlett<sup>50</sup> and others) investigated the extent to which the decomposition reaction in treated vessels is inhibited by the addition of propylene, *n*-hexane, and other inhibitors. In all cases where an inhibiting effect was observed, the velocity of reaction changed by 3 to 4 times in the presence of additives. Recently, we undertook an investigation into the action of propylene in clean vessels. It turned out that, in this case, inhibition is considerably more intense (20 times more marked). This difference in itself makes the general idea of the retarding action of propylene being connected with a chain termination in the gas phase, somewhat doubtful.

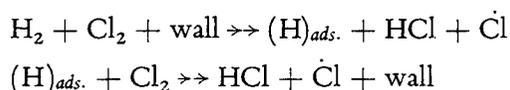
An exhaustive investigation of this question using differential calorimetry would appear to point to the fact that, in any case, the main proportion of inhibition (80 to 90%) is not connected with chain termination in the gas phase but with the suppression of chain formation at the walls, due to adsorption of propylene.

These results can be considered as a certain confirmation of the hypothesis of V. V. Voevodskii<sup>51</sup> regarding the action of NO admixtures on hydrocarbon cracking. In accordance with the comments of F. O. Rice and K. F. Herzfeld<sup>52</sup>, Voevodskii assumes that the hydrocarbon chains form and break at the walls in the cracking process too. In his opinion, the nitrogen oxide inhibits the initiating action of the walls. These experiments to find a new solution to this question are connected with the fact that the acknowledged opinion of Sir Cyril Hinshelwood<sup>53</sup> on the nature of inhibitions in the cracking reaction, although it does offer some advantages, can only with difficulty explain certain test results. For example, some authorities<sup>54</sup> have shown that, in the case of reactions in the presence of molecular deuterium or stable deuterium compounds, the deuterium content of the reaction products is roughly the same in non-inhibited as in reactions inhibited by NO.

We set ourselves the task of investigating the mechanism of the formation of free radicals on solid surfaces. We consider it probable that, in solid bodies and particularly on their surface, there are free valences<sup>35</sup>. These can be considered in a similar light to the free radicals and therefore, their action on the molecule emerging from the gas phase has a low activation energy. The molecule decomposes: one of the radicals saturates the surface valence, becomes chemisorbed, and the other passes over into the gas phase.

The trapping of the free radical on the wall occurs by its chemisorption, but one or other bond in the solid is ruptured and at the same time, a new free valence forms on the surface. For this reason, these processes do not change the total number of free valences (neither on the wall nor in the volume); free valences are destroyed only as the result of their interaction.

Free valences can probably be created by the solid bodies being especially prepared. At high temperatures, they may occur spontaneously due to thermal movement. Also, the possibility of their formation through the release of energy in chemical reaction processes on the surface is not excluded, for example:



With such a formation of two chlorine atoms, 15 kcal instead of 57 kcal are consumed in dissociation of the chlorine molecule in the gas phase.

The ideas indicated regarding the mechanism of the share which the wall has in initiating and terminating chains as yet remain very hypothetical. We have endeavoured to connect them with the properties of the semi-conductive solid bodies<sup>55</sup>. The qualities of the current carriers in the semi-conductors - the free electrons and the pores - are namely very similar to the properties of the free valences on the surface, as postulated by us, both having as they do the characteristic quality of the free radicals - they have an odd number of electrons. Taking quite a rough approximation, the electron and the pore in the semiconductor lattice (e.g. ZnO) can be equated to the ions of the radical (Zn<sup>+</sup> and O<sup>-</sup>).

In line with this analogy, we assumed in 1953 that the free valences on the wall did not alone contribute to ejecting the radicals into the gas phase, but also played a substantial role in the mechanism of heterogeneous catalysis in the redox processes. Some schemes have been suggested which describe in a fully satisfactory way the progress of some complicated catalytic reactions, for example the chain scheme of the synthetic process of CO + H<sub>2</sub>.

At the moment, there are still no direct test results which confirm the radical mechanism or the ion-radical mechanism of the redox processes. However, there are quite a number of observations which provide indirect confirmation. The fact must be emphasized particularly that the greatest number of redox catalysts are semiconductors and metals<sup>56</sup>. On the other hand, quite a lot of data has been collected relative to comparative investigations into the electrical conductivity and catalytic properties of semiconductors. All these data point to the fact that these two categories of properties are closely linked with each other. A particularly clear indication of this is the effect produced by addition of small quantities of ions of a different valence into the semiconductor lattice (e.g. Li<sup>+</sup> and Cr<sup>3+</sup> into the lattice of Zn<sup>2+</sup>O<sup>2-</sup>, Ni<sup>2+</sup>O<sup>2-</sup>, etc.); when this happens, the electrical conductivity undergoes a sharp change, just like the catalytic activity, becoming either greater or smaller. Any admixture which influences the electrical conductivity also always causes changes in the catalytic activity. Sometimes, these changes occur in one and the same direction, but sometimes in an opposite direction, depending upon the type of reaction, the properties of the admixtures, the p- or n-character of the semiconductor and upon the temperatures. Although as yet we have no detailed theory at our disposal which is capable of describing all these data, it can probably be asserted that such a theory

must be founded on an exact picture of free surface radicals and such a theory would enable us, working from a uniform standpoint, to combine both the electrical and the catalytic peculiarities of the process.

We would like to mention here that, also with the acid and base catalysts, as N. M. Chirkov has shown, a connection exists between the electrical conductivity and the catalytic properties, but this connection is of quite a different kind. In 1947, we found<sup>57</sup> that in the presence of small quantities of hydrochloride gas and water vapours, surface plates of mica, quartz and glass acquired marked properties of acid-base catalysts. The esterification reaction and decomposition of paraldehydes were thoroughly investigated, and it became manifest that the surface electrical conductivity changes in parallel with the catalytic activity. Further investigations showed us that the reaction in the adsorption layer (which contains either one or a few layers of molecules) takes place largely just as in the acidified liquids.

The main outcome of many years' work by various chemical-kinetic schools is the certainty that a large number of chemical reactions in the gas phase and also by far the majority in the liquid and solid phase, as well as the heterogeneous catalytic reactions on solid surfaces, are aided by particularly labile intermediate forms which are produced during the course of the process. These labile intermediate forms have a considerably greater reactivity than even the least stable molecules with saturated valence bonds.

The development of theoretical and experimental processes of investigating these labile intermediate forms must be regarded as the most important task for the immediate future. We must clearly tie up the properties of these labile intermediate forms with their chemical structure or the structure of the molecules from which these labile forms are produced. We must clarify in detail how the process itself can generate such labile intermediate forms and so secure its own auto-development.

I see the value of the chain theory first of all in that it has succeeded, taking examples from gas reactions, in developing general notions relative to the simplest labile forms corresponding to these reactions - the free atoms and radicals. In a few cases, it has been possible to show that the doctrine relating to chain reactions constitutes an applicable theory which makes it possible quantitatively to foretell the astonishing wealth and manifold courses of the reaction processes which are characteristic even of such simplest chain processes as the formation of water from hydrogen and oxygen.

The chain theory makes it possible to come nearer to the solution of a

main problem in theoretical chemistry - the connection between reactivity and the structure of the particles entering into the reaction.

For chain processes, the reaction of free radicals with the molecules is characteristic (the reaction of chain propagation). Such reactions belong to the simplest because here only one bond is disrupted and one bond is generated afresh. Therefore, the investigation of these simple reactions offers the best opportunity for breaking fresh ground in the development of the theory of reactivity and it can be applied subsequently to other types of reaction also.

It is one of the main tasks of chemistry to create a possibility of rationally regulating the rate and direction of a chemical change. Unfortunately, chemistry and the chemicals industry are in this respect lagging behind radio technology, electronics, atomic engineering, etc., where technology is based far more on theoretical anticipation and calculation. The chain reaction theory shows the first possibilities in this respect also.

That the chain reaction includes the stages of initiation of the chain and its termination, which are greatly dependent upon the average condition and upon external influences, opens up the possibility of regulating the rate and sometimes even the yield of the process. The knowledge of the reaction of chain propagation often makes it possible to control the process in the desired direction.

Accordingly, the chain theory provides fresh prospects of perfecting established industrial processes and others which are new and in the development stage, and is already to a certain extent being applied; this is particularly true with polymerization processes.

One of the next tasks is the application of the notion of chain theory to the development of new technology of direct oxidation processes and hydrocarbon cracking. I would like further to add that, for practical purposes of chemical technology, radioactive radiation probably offers very good prospects where chain reactions are concerned.

Certainly, chemical transformation processes are not limited purely to radical chain reactions which occur with the help of free radicals; a vast number develop with the help of quite different labile forms.

I am firmly convinced that it is entirely necessary to extend the research into the mechanism of various types of chemical reactions. It is hardly possible to enrich chemical technology to any extent without this knowledge or even to achieve decisive success in biology.

Naturally, there are considerable obstacles in the way. The chemical pro-

cess is the basic phenomenon which makes chemistry different from physics and makes the former a more complicated science. The development of the theory of a chemical process is also considerably more difficult than the development of the theory of chemical structure.

More than anywhere, the mutual endeavours of learned men in every country are needed in the resolution of this most important problem, in order to explain the secrets of chemical and biological processes, to the benefit of peaceful development and the well-being of mankind.

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