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On the Kinetics of Complex Reactions*

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Chemical kinetics is the chemistry of intermediate compounds. These intermediates can be studied directly only with great difficulty but they can be investigated through kinetic measurements themselves. For example during the induction period in the oxidation of hydrogen sulfide the "active centers" are withdrawn from the reaction vessel passed through a connecting vessel and introduced into a chamber in which the new reaction is just starting. The "active centers," responsible for shortening the induction period, are stable for several hours at room temperature. The formula previously given for a chain reaction proceeding from a single active center is extended here to include reactions with any number of active centers. Complex reactions of various types are treated mathematically and experimental curves are given. Among the types of complex reactions considered are those which involve the mutual inhibiting or promoting action of chains with quadratic rupture.

§1. PRESENT PROBLEMS IN CHEMICAL KINETICS

IN the early twenties of this century chemical kinetics began to develop at a quite astonishing rate. During this period was developed the theory of chain reactions which plays such an important part in the study of complex reactions, as well as the theory of the activated complex which has so satisfactorily solved the problem of the kinetic analysis of the simpler reactions and of the elementary stages of the more complex reactions. However, in the course of the last two or three years, the development of chemical kinetics has slowed down partly because the workers in this field shrink from the immense difficulties in the way of its further development.

Chemical kinetics should not be treated as a branch of physical chemistry. Chemical kinetics represents an entirely new domain of science equal in scope to the domains embraced by inorganic, organic and physical chemistry taken together. It differs essentially from chemistry in that it deals, not with the properties of stable compounds and their structure, but with the chemical process itself, however, complex it may be. Its relation to chemistry is more or less the same as that of physiology to anatomy.

Every chemical process comprises a number of stages, proceeding by various unstable compounds which heretofore have been left out of account by chemistry because of their lack of stability. Chemical kinetics might rightly be called the chemistry of intermediate compounds. One of the most important and most difficult problems of chemical kinetics consists in the development of simple and reliable methods of analyzing these intermediate compounds in their different stages of reaction. It is the lack of stability and the extreme difficulties inherent in the existing methods which are responsible for the slowing down of the progress of chemical kinetics.

The study of the intermediate compounds consists mainly in taking samples of the reacting mixtures, cooling them rapidly and then proceeding to their chemical analysis. Many difficulties arise: (1) A great number of the intermediate compounds lack stability at room temperature and cannot be kept for the time required for analysis. (2) The microanalytical methods are rather cumbersome and not sufficiently reliable especially in the case of complex mixtures. (3) In the analysis, all the compounds have to be determined, including the side-products, and we have no criterion for choosing those substances which are responsible for the course of the reaction.

The analysis of intermediates has not been used extensively enough, and new improvements should be developed. Attention might be drawn, in this respect, to some attempts at making use of the polarographic method of Heyrovsky.¹ I wish to give here (Table I) one of the polarograms

^{*} This article was communicated to the symposium on "The Kinetics of Homogeneous Gas Reactions," but was not available in time for publication in the preprints. See page 633.

¹ I. J. Heyrovsky, Theory and Practice of the Polarographic Method.

	C ₂ H ₅ OOH	CH2O	C3H6O	
The mixture contained The polarogram yields	0.00264% 0.00264%	0.0318% 0.0292%	0.00715% 0.00697%	

TABLE I.

obtained at our Institute by Stern and Pollak² (Fig. 1).

Professor Sokolik of our Institute and his coworkers are now adapting the method to the analysis of the intermediate products formed during the pre-flame period which are responsible for inflammation and detonation in bombs, tubes and internal-combustion engines.

With the aid of the above method Professors Neumann and Dobrinskaja³ have investigated the increase in the amount of peroxides and aldehydes during the induction period preceding the formation of a cold flame in mixtures of butane and oxygen. The results obtained at a temperature of 310°C and a pressure of 333 mm Hg are given in Fig. 2. Curve 1 shows the variation of the pressure in the mixture with the time, the moment of the formation of the cold flame being marked by an arrow. A special highly-sensitive membrane manometer did not show any variation of pressure during 32 seconds; however, the polarographic analysis of samples of the gas showed a continuous increase in the amount of aldehydes (curve 2) and of peroxides (curve 3, drawn on a scale 10 times as great as that of curve 2). Plotting the logarithm of the aldehyde concentration, a linear increase with the time is obtained (curve 4). This means that, in accord with the theory, the amount of aldehydes increases as $e^{\phi t}$. The polarographic method can thus be applied when the partial pressure of the aldehyde or the peroxide in the mixture is less than 0.1 mm or 0.01 mm Hg, respectively.

Among the physical methods of analysis we might mention that based on the study of absorption spectra. Quite recently Professor Kondratiew of our Institute was able to detect by this method the presence of CS radicals in the cold flame of carbon disulphide. For the study of the extremely unstable products of the type of radicals one might recommend the method of "line spectra" emitted by the products examined, which has been proposed and developed by Kondratiew, and successfully applied by Kondratiew and Avramenko to the analysis of OH in a "cold" hydrogen flame.

However, for different reasons, the absorption method can be applied only in a limited number of cases. Still more limited in its application is the investigation of complex reactions by means of the heavy hydrogen and oxygen isotopes or the artificial radioactive isotopes, though these methods sometimes lead to quite new and important results. Thus Professor Roginsky, of our Institute, and co-workers have found with the aid of radioactive indicators that the monosolvate exchange proceeds in many cases very slowly. They also investigated the kinetics of this process. Professor Roginsky was also able, by using the same method, to throw more light on the mechanism of the catalysis by aluminium bromide.

The mass-spectrograph method appears also to be suitable for the analysis of the intermediate products. However, our attempts in this respect have proved a failure. Neither the physical nor the chemical methods are thus seen to yield simple and reliable means for the analysis of the intermediate products, though in many cases they prove quite helpful and should be developed.

I believe, however, that in general the more universal methods should not be borrowed from other branches of science, but should be based on the principles of chemical kinetics itself. To illustrate the possibility of such methods, I wish to describe here the results of a few experiments which have been recently undertaken by Emanuel and myself.

In the initial stages of any self-accelerating reaction the amount of the substance having undergone reaction varies with the time accord-



² Stern and Pollak, Acta Physicochim. 7, 567 (1937).

⁸ A. A. Dobrinskaja and M. B. Neumann, Acta Physicochim. **10**, 297 (1939). The electrolyte was 1/20 N LiCl.



ing to the law

$$x = A(e^{\phi t} - 1) \simeq A e^{\phi t}.$$

The amount of x can be detected with the aid of an apparatus of a given sensitivity only after a time-interval τ_1 (called "induction period") when it has already attained a definite value x_0 . It follows from the theory that the addition of an active product will result in a decrease of this induction period, and it is on this fact that our method has been based.

A mixture of H_2S and O_2 was kept in the vessel 1 (Fig. 3) during a time-interval t_1 (less than the period of induction τ_1 corresponding to the given temperature and pressure) and was then transferred to the vessel 2 maintained at the same temperature. In the vessel 2 the period of induction τ_2 decreases in comparison with its normal value τ_2^0 . The experimental relationship between t_1 and τ_2 is shown in Fig. 4. Midway between the vessels 1 and 2 the glass vessel Rwas placed, kept at room temperature. The mixture, before being admitted to the vessel 2, remained for a certain definite time θ in the vessel R. In our experiments, t_1 was constant and equal to τ_1 (the total induction period). The experimental relationship between θ and τ_2 is shown in Fig. 5. The active centers are seen to be extremely stable at room temperature and to live for several hours.

The relationship between τ_2 and the relative concentration *C* of the active centers can now be established by diluting the mixture in *R* which contains a definite number of active centers, with a fresh supply of the mixture, this relationship is shown in Fig. 6. With the aid of the above curve which presents a calibration curve of the given analyzer, we are able to eliminate τ_2 from the curves 4 and 5, and thus answer the following questions: (1) How the relative concentration of the active centers in vessel 1 increases with the time. (2) How the active centers are destroyed in vessel *R* at room temperature.

The corresponding curves are shown in Fig. 7 and Fig. 8. If $\log C$ is plotted instead of the concentration C, fairly straight lines are obtained. This means that (1) in accord with the theory, the accumulation of the active products during the induction period obeys the law $e^{\phi t}$, and (2) that the destruction of the active products at room temperature follows a monomolecular law proceeding in a homogeneous way as established by varying the ratio of surface to volume for vessel R. The above purely kinetic method of analysis, together with chemical and physical methods, will enable us, we hope, to fully investigate the nature of the active products, and not only to find the mass of the product by using, for instance, the diffusion through a small aperture in the membrane, but also to determine its chemical composition and structure by studying its interaction with various reactants in vessel R. Irrespective of the relative value of the method proposed, the possibility of developing new purely kinetical methods for the analysis of the intermediate products is not to be doubted.



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The development of reliable methods for the analysis of the intermediate products forms thus one of the main problems of chemical kinetics awaiting solution. But it is not alone the lack of suitable methods which impedes the progress of chemical kinetics. The classification of the chemical reactions according to their formal over-all



FIG. 4.

kinetics remains one of the main problems of this branch of science, and very little has been done in this respect during the last three years.

As before, research is restricted to a few simple reactions, such as H_2+Cl_2 , H_2+O_2 , CH_4+O_2 etc., and yet we have no definite knowledge of their kinetics and much less of the mechanism of the reaction. Very often contradictory results are reported by the different authors, and a generalization of the whole experimental and theoretical data available for any of the above mentioned reactions is still lacking. If this state of things persists, it will be long before chemical kinetics obtains the necessary solid foundations for its further development.

It must also be noted that the number of reactions investigated does not widen. It would be timely to proceed to the kinetic investigation of other types of reactions, but we are immediately confronted with several essential difficulties. Thus, for any reaction other than the oxidation processes there have never been observed inflammation limits having the character of chains, at least as far as the upper limit is concerned. It would be hard to believe that the phenomenon is restricted only to oxidation processes. Recently Appin, of our Institute, found characteristics of the upper limit in the inflammation of nitrogen

TABLE II.*

TEMPERATURE	p_2
÷ر	MM HG
20	40
40	70
60	115

* The saturated vapor pressure of NCls at 20°C is 150 mm Hg.

chloride vapor. Above a definite pressure p_2 , the vapor did not decompose, appreciably, for many days over a range of temperatures from 0 to 50°; but at pressures below p_2 , self-inflammation was observed. The lower limit was either entirely absent or else it lay below 0.01 mm, since even at this pressure the inflammation of the NCl₃ vapor was quite distinct. Table II gives the values of the upper limit p_2 for different temperatures.

Upon the addition of air, the upper limit decreased gradually and, upon a definite dilution, the NCl₃ vapor became practically uninflammable. This appears to indicate that the chainlike inflammation is not limited to oxidation processes alone.

I would like to point out still another circumstance. Some of the workers apparently lack a clear understanding of the fundamental statements of the theory of chain reactions and of the deductions to which it leads. This is sometimes felt when the general laws which, in my book, have been deduced for the case of one single active center are applied to reactions proceeding with a greater number of active centers and also in cases where the rupture and branching are connected with the mutual action of the intermediate products. These two problems were



not sufficiently elucidated in my book. During the last few years I have developed a complete theory of complex reactions taking into account the disappearance of the initial products by combustion and the self-catalysis by the final products. It should be timely to discuss these problems at the present symposium. Space limitations compel me to restrict myself to the examination of the problems concerning the analysis



of the initial stages of the reaction, leaving aside the more complicated problem of accounting for the disappearance of the initial products by combustion and the self-catalysis by the final products.

§2. Complex Reactions Linear with Respect to the Concentration of the Initial Products

If m different intermediate products participate in the reaction, their respective concentrations n_i will be determined by a system of mdifferential equations of the type

$$dn_{i}/dt = n_{0}^{(i)} + C_{1i}K_{1}n_{1} + C_{2i}K_{2}n_{2} + \cdots + C_{i}K_{i}n_{i} + \cdots + C_{mi}K_{m}n_{m}, \quad (I)$$

where $n_0^{(i)}$ is the rate at which the centers n_i are generated spontaneously, at least in one of the above *m* equations. The term $n_0^{(i)}$ differs from zero. The values of the coefficients C_{ij} are either zero or positive, their order of magnitude being close to 1 or to 2, at the utmost. The values of the coefficients C_i are also positive and always exceed 1.

The above system possesses stationary solutions, proportional to the number n_i^0 of the



centers generated (if one kind of centers is generated), if the determinant D of the homogeneous system satisfies the inequality

$$(-1)^{m+1}D < 0.$$
 (1)

For $(-1)^{m+1}D > 0$, nonstationary solutions are obtained and the concentrations n_i increase with the time. The solution of the characteristic equation $D(\lambda) = 0$ yields *m* roots, out of which (m-1)roots are represented either by negative values or by complex quantities with negative real parts. The remaining root $\lambda = \phi$ which, as a rule, is the smallest as regards its absolute value, is either negative, if $(-1)^{m+1}D < 0$, or positive, if $(-1)^{m+1}D > 0$.

This means that for not too small values of t the concentrations of the centers are proportional to $e^{\phi t}$ and therefore to each other. If n_i^0 are the particular solutions of the system (putting $dn_i/dt=0$), we may expect that to a sufficient degree of precision

$$n_i = |n_i^0| (e^{\phi t} - 1). \tag{3}$$

If $(-1)^{m+1}D < 0$, then it may be expected that

$$n_i = n_i^0 (1 - e^{-|\phi|t}), \qquad (4)$$

though with a lesser degree of precision (owing



to the smaller absolute value of the root $\lambda = \phi$). If $(-1)^{n+1}D < 0$, the values of n_i^0 determine those concentrations of the intermediate products which will be established with the time, i.e., the stationary concentrations. The values of n_i^0 are all inversely proportional to |D|. The reaction rate which presents a definite linear combination of the values $C_i K_i n_i$ is also inversely proportional to |D|. If certain conditions are satisfied concerning the order of magnitude of the different K_i , then the value of the smallest root ϕ will also be approximately porportional to D.

The determinant $(-1)^{m+1}D$ can always be represented in the form of some quantity proportional to the difference $\delta - \beta$ (the probability of branching minus that of rupture). Thus the stationary reaction rate $w = Cn_0/(\beta - \delta)$. The nonstationary reaction rate as a function of the time is

$$w = \frac{n_0}{\delta - \beta} (e^{\phi t} - 1). \tag{5}$$

In many cases presenting some interest from a practical point of view, $\phi C(\delta - \beta)/\tau$, where τ is the time during which the slowest link develops, *C* being a positive integer.

For any complex reaction, the condition for the transition from a stationary to a nonstationary régime reads $\delta - \beta = 0$. In a number of cases (but not all) δ and β are simple functions of the temperature.

Thus it can be said that all the expressions obtained earlier⁴ for the simplest case of a chain reaction proceeding with the aid of one single active center will also hold more or less accurately in the case of reactions with any arbitrary number of active centers.

Example 1

Monocyclic system with three centers.—

$$dn_{1}/dt = n_{0} - (K_{1} + K_{1}')n_{1} + LK_{3}n_{3} = n_{0} - A_{1}K_{1}n_{1} + LK_{3}n_{3},$$

$$dn_{2}/dt = K_{1}n_{1} - (K_{2} + K_{2}')n_{2} = K_{1}n_{1} - A_{2}K_{2}n_{2},$$

$$dn_{3}/dt = K_{2}n_{2} - (K_{3} + K_{3}')n_{3} = K_{2}n_{2} - A_{3}K_{3}n_{3}.$$

(II)

Here $K_1'n_1$, $K_2'n_2$, $K_3'n_3$ are the rates at which the chains are broken.

The value of L can be equal either to zero (complex reaction without chains), or to 1 (simple chain reaction), or to 2 (branching chain). A_1, A_2, A_3 are always greater than 1.

$$(-1)^{\varepsilon+1}D = D = K_1K_2K_3\Delta,$$

where

$$\Delta = \begin{vmatrix} -A & 0 & L \\ 1 & -A_2 & 0 \\ 0 & 1 & -A_3 \end{vmatrix} = L - A_1 A_2 A_3. \quad (6)$$

For D < 0, the stationary solutions are

$$n_{1}^{0} = \frac{n_{0}}{A_{1}K_{1}} \frac{A_{1}A_{2}A_{3}}{A_{1}A_{2}A_{3} - L};$$

$$n_{2}^{0} = \frac{n_{0}}{A_{1}A_{2}K_{2}} \frac{A_{1}A_{2}A_{3}}{A_{1}A_{2}A_{3} - L}, \quad \text{etc.},$$
(7)

the nonstationary solutions, for D > 0, being

$$n_1 = \frac{n_0}{A_1 K_1} \frac{A_1 A_2 A_3}{L - A_1 A_2 A_3} e^{\phi t}, \qquad (8)$$

the reaction rate being

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$$v = A_1 K_1 n_1 + A_2 K_2 n_2 + A_3 K_3 n_3.$$

 $1/A_1 = \alpha_1$ is the probability that the chain will continue at the first link, $1/A_2 = \alpha_2$ the probability that it will continue at the second, $1/A_3 = \alpha_3$, at the third link, while $1/A_1A_2A_3$ $= \alpha_1\alpha_2\alpha_3 = \alpha$ is the probability that the chain will be continued after a complete cycle. If L = 1, then $(A_1A_2A_3 - 1)/A_1A_2A_3 = 1 - \alpha = \beta$ is the probability of a rupture after a complete cycle. Hence $w \leq n_0/\beta$. Since Δ is always <1, any nonstationary solutions are excluded.

For L=2, $(A_1A_2A_3-2)/A_1A_2A_3=\beta-\alpha$, and since in the case of a continuously branching chain $\alpha=\delta$, the quantity $\beta-\alpha$ will be equal to $\beta-\delta$. In this case nonstationary solutions are also possible, considering that $L-A_1A_2A_3$ can be >0.

It is easily seen that, if $A_1K_1 \ll A_2K_2$ and $\ll A_3K_3$, then

$$\phi = \frac{A_1 K_1 (2 - A_1 A_2 A_3)}{A_1 A_2 A_3} = \frac{\delta - \beta}{\tau}, \qquad (9)$$

where $\tau = 1/A_1K_1$, is the time during which the slowest link develops, being approximately the time during which the complete cycle develops,

⁴ N. Semenoff, *Chemical Kinetics and Chain Reactions* (Oxford University Press, 1935), Part. I.

since $1/A_1K_1 \gg 1/A_2K_2$, and $1/A_3K_3$. Hence

$$n_1 = \frac{n_0 \tau}{\delta - \beta} (e^{(\delta - \beta/\tau)t} - 1).$$

It must be noted that this approximate solution corresponds to that which is obtained in system I when putting $dn_2/dt = dn_3/dt = 0$. This approximate method of solution will be satisfactory if $A_1K_1 \ll A_2K_2$ and A_3K_3 .

The general aspect of the determinant of this or another complex reaction shows at once the most convenient form of diagram by which to illustrate the system. The above scheme is best represented as in Fig. 9, the diagram being selfexplanatory.

Example 2

Bicyclic system with three centers.—A number of schemes of this type are shown in Figs. 10, 11 and 12, all three leading to similar results from a kinetical point of view.

Let us examine the scheme 10, Its equations are:

$$dn_{1}/dt = n_{0} - A_{1}K_{1}n_{1} + K_{2}n_{2} + K_{3}n_{3},$$

$$dn_{2}/dt = K_{1}n_{1} - A_{2}K_{2}n_{2},$$

$$dn_{3}/dt = K_{2}n_{2} - A_{3}K_{3}n_{3}.$$

(III)

The determinant

$$D = K_1 K_2 K_3 \Delta,$$

where

$$\Delta = \begin{vmatrix} -A_1 & 1 & 1\\ 1 & -A_2 & 0\\ 0 & 1 & -A_3 \end{vmatrix} = 1 - A_3 (A_1 A_2 - 1). \quad (10)$$

Let us denote by D_1 the minor of the determinant D. Then $D_1 = K_1 K_2 \Delta_1$; $\Delta_1 = A_1 A_2 - 1$. This minor corresponds to the determinant of the chain reaction of the first cycle alone of the given bicyclic system (10). The precise solution of the above system of equations yields the following rule for obtaining an approximate expression for the value of ϕ in the expressions $n_i = n_i^0(e^{\phi t} - 1)$ determining the variation of the concentration n_i with the time in the case of a nonstationary régime (D > 0).

(a) If
$$A_2K_2 \gg A_1K_1$$
 and A_3K_3 , and
 $DA_2K_2/D_1^2 \ll 1$, (11)

then we may put $dn_1/dt = dn_2/dt = 0$ in solving the system (III). At the same time

$$\phi = K_3 \Delta / \Delta_1. \tag{12}$$

(b) If
$$A_2K_2 > A_1K_1$$
 and A_3K_3 and

$$D/A_{2}K_{2}(A_{3}K_{3})^{2} \ll f,$$
 (13)

then in solving the system (III) we may put $dn_2/dt = dn_3/dt = 0$. At the same time

$$\phi = K_1 \Delta / A_2 A_3. \tag{14}$$

For D < 0, the stationary solutions are:

$$n_{3}^{0} = \frac{n_{0}}{A_{1}A_{2}A_{3}K_{3}} \frac{A_{1}A_{2}A_{3}}{A_{3}(A_{1}A_{2}-1)-1}, \text{ etc.} \quad (15)$$

If the first cycle of the bicyclic system be looked upon as the fundamental chain, then $1-1/A_1A_2=\beta$ is the probability of rupture. The probability of the continuation of the second cycle $\alpha = 1/A_1A_2A_3$ will at the same time represent the probability of branching with respect to the fundamental chain. Hence

$$\frac{A_1A_2A_3}{A_3(A_1A_2-1)-1} = \frac{1}{\beta-\delta}.$$

The stationary reaction rate $w = C(n_0/\beta - \delta)$ where C is of the order of 1.

In the case of a nonstationary reaction

$$w = C \frac{n_0}{\delta - \beta} (e^{\phi t} - 1).$$

If the fundamental chain is sufficiently long and the branchings few, then $K_1' \ll K_1$, $K_2' \ll K_2$, $K_3 \ll K_3'$. Hence

$$\delta = \frac{1}{A_1 A_2 A_3} \underbrace{\simeq}_{K_3'}^{K_3} \text{ and } \beta = 1 - \frac{1}{A_1 A_2} \underbrace{\simeq}_{K_1}^{K_1'} + \frac{K_2'}{K_2}.$$

Since all the values K are temperature functions of the type $e^{-E/RT}$, it follows that one of the ratios K_1'/K_1 and K_2'/K_2 will be considerably greater than the other. Thus in the case of long chains with few branches β and δ are simple temperature functions of the type $e^{-E/RT}$.

The value of ϕ in expression (11) is equal to

$$\phi = \frac{K_3 \Delta}{\Delta_1} = \frac{A_3 K_3 (\delta - \beta)}{\beta} = \frac{\delta \gamma - 1}{\theta}, \quad (16)$$

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where γ is the length of the fundamental chain, and θ , the time required for the branching, is great in comparison with the time required for the development of the fundamental chain, since the condition (11) will be satisfied only if

$$DA_{2}K_{2}/D_{1}^{2} = K_{3}\Delta A_{2}/K_{1}\Delta_{1}^{2} \ll 1.$$

Thus we are dealing with a case of "degenerate branching," as it has been called in my book.



It can be easily seen that expression (16) is identical with that given in my book.

In case (b) according to (14)

$$\phi = \frac{K_1\Delta}{A_2A_3} = \frac{A_1K_1\Delta}{A_1A_2A_3} = \frac{\delta - \beta}{\tau},$$

where τ is the time required for the development of the first cycle (since $1/A_1K_1 \gg 1/A_2K_2$). Thus a formula is obtained similar to that given in my book for chains where the branching does not proceed more slowly than the development of the fundamental chain.

The following conclusions can thus be drawn.

(1) For any complex reaction, the transition of the stationary to the nonstationary state is determined by the condition D=0 which is equivalent to $\beta-\delta=0$.

(2) In the case of a nonstationary state, however complex the reaction may be, the reaction rate (for values of *t* that are not too small) is always expressed by a function of the type $e^{\phi t}$, and the concentrations of all the intermediate products are proportional to each other.

(3) In most of the complex reactions presenting some interest from a practical point of view, if the branching does not proceed considerably more slowly than the development of the fundamental chain $\phi = (\delta - \beta)/\tau$, while in the case of degenerate branching $\phi = (\delta \gamma - 1)/\theta$.

(4) For long chains with few branchings, β and δ are simple functions of the temperature of the type $e^{-E/RT}$.

(5) In the case of schemes that are not too complex-having but two or three kinds of

centers—the reaction is best characterized by the values of β and δ . In the case of still more complex schemes, the values A and L are more appropriate.

§3. MUTUAL INHIBITING ACTION OF THE CHAINS. QUADRATIC RUPTURE

If the rupture of the chains is due not only to the interaction of the active centers with the wall or with the initial products (rupture of the linear type), but if in addition some of the centers perish owing to recombination or to some other kind of mutual action, then the system of equations determining the course of the reaction ceases to be linear. We shall restrict ourselves to the examination of one single case where only one of the centers perishes owing to recombination at a rate Bn_1^2 .

(a) Quadratic rupture in a monocyclic system

$$dn_{1}/dt = n_{0} - A_{1}K_{1}n_{1} + LK_{3}n_{3} - Bn_{1}^{2},$$

$$dn_{2}/dt = K_{1}n_{1} - A_{2}K_{2}n_{2},$$
 (I)

$$dn_{1}/dt = K_{2}n_{2} - A_{3}K_{3}n_{3}.$$

For the solution of the above system of equations the same determinant will be of use, as for the purely linear scheme of §2.

 $D = K_{*}K_{*}K_{*}\Lambda$

where
$$\Delta = \begin{vmatrix} A_1 & 0 & L \\ 1 & -A_2 & 0 \\ 0 & 1 & -A_3 \end{vmatrix} = L - A_1 A_2 A_3.$$
 (1)

If $\Delta < 0$, the system has a stationary solution, namely,

$$n_1 = \frac{2n_0}{(F^2 + 4Bn_0)^{\frac{1}{2}} + |F|},$$
 (2)

where $F = A_1 K_1 \Delta / A_1 A_2 A_3$ is <0, |F| denoting the absolute value of F. For low values of n_0 , expression (2) reduces to

$$n_1 = \frac{n_0}{|F|} = \frac{n_0}{A_1 K_1} \frac{A_1 A_2 A_3}{|\Delta|}, \qquad (2')$$

this being the same solution as for the system of linear equations.

If $\Delta > 0$, the linear system led to an infinitely autoaccelerating reaction, now this increase is

limited by the quadratic term; another stationary solution is thus obtained, independent of n_0 (for low values of n_0) and corresponding to concentrations and velocities much higher than those for $\Delta < 0$.

In this case $\Delta > 0$ and $F = A_1 K_1 \Delta / A_1 A_2 A_3 > 0$,

$$n_1 = \frac{2n_0}{(F^2 + 4Bn_0)^{\frac{1}{2}} - F},\tag{3}$$

which, for low values of n_0 , yields

$$n_1 = \frac{F}{B} = \frac{A_1 K_1 \Delta}{A_1 A_2 A_3 B}$$
(3')

and the reaction rate

$$w = K_1 n_1 = A_1 K_1^2 \Delta / A_1 A_2 A_3 B.$$

If $A_1K_1 \ll A_2K_2$ and A_3K_3 , the solution of the system can be obtained by putting $dn_2/dt = dn_3/dt = 0$, whence

$$dn_1/dt = n_0 + Fn_1 - Bn_1^2$$
 (II)

which for $\Delta > 0$ gives

$$n_1 = \frac{2n_0(e^{\sqrt{q} t} - 1)}{(\sqrt{q+F}) + (\sqrt{q-F})e^{\sqrt{q} t}},$$
 (4)

where

For small vales of n_0 , the above expression reduces to

 $q = F^2 - 4Bn_0.$

$$n_1 = (n_0/F)(e^{Ft} - 1)$$
 (5)

for low values of t, and to $n_1 = F/B$, for high values of t.

Thus, at the beginning of the process until the stationary velocity has been attained, the increase of n_1 , and therefore the increase of the reaction rate, obeys the same law as in the case of a linear scheme; in the course of time this increase slows down, leading to a constant concentration F/B and a constant velocity.

Thus, if the stationary reaction rate is so high that the reaction changes to thermal explosion even before this velocity has been attained, then the quadratic rupture can be neglected; it suffices then to examine only the linear scheme, assuming as before, that the condition A=0continues to determine the transition to a nonstationary régime.

Such is the case for rapid reactions (inflammation). Indeed, for a recombination of the type $H+H+M=H_2+M$, the constant B is of the order of $10^{-32} \times 10^{18} = 10^{-14}$ at pressures of the order of 1/10 of an atmosphere. In order that the reaction rate K_1^2/B be low, of the order of 10^{14} molecules per second, the value of $1/K_1$ must be equal to about one second. For such low developments of the link of the chain and for low values of n_0 , the delay of inflammation should be of the order of tenths of a minute, but for the H_2+O_2 reaction this is different. Thus Kowalsky found $1/K_1$ equal to about 1/10th of a second at a pressure of ~ 1 mm. At a pressure of 100 mm, $1/K_1$ would therefore attain $\sim 10^{-3}$ sec. If we put $K_1 = 10^3$, the reaction rate K_1^2/B becomes $\simeq 10^{6}/10^{-14} \simeq 10^{20}$ molecules per second and is practically infinite.

Thus, when examining the upper and lower limits for rapidly-proceeding reactions of the type H_2+O_2 , the quadratic ruptures can be left out of account though they are often present.

(b) Quadratic rupture in polycyclic schemes

Let us examine a scheme of this kind, as illustrated in Fig. 11, but showing in addition a quadratic rupture at the right lower corner.

$$dn_1/dt = n_0 - A_1 K_1 n_1 + L K_2 n_2 + K_3 n_3, dn_2/dt = K_1 n_1 - A_2 K_2 n_2, dn_3/dt = K_2 n_2 - A_3 K_3 n_3 - B n_3^2.$$
 (III)

The determinant of the linear part of the scheme is

$$\Delta = LA_3 + A_2 - A_1A_2A_3 = A_2 - (A_1A_2 - L)A_3. \quad (6)$$

The determinant of the first cycle $n_1 - n_2 - n_1$ is

$$D = K_1 K_2 K_3 \Delta_1$$
 where $\Delta_1 = (A_1 A_2 - L).$ (7)

If $\Delta_1 > 0$ and $\Delta < 0$, the stationary solution, for low values of n_0 , is

$$n_3 = \frac{n_0}{|\Delta|} \frac{A_1 A_2 A_3}{A_1 A_2}, \tag{8}$$

i.e., the same as for a scheme without quadratic rupture. If $\Delta_1 > 0$ (occurring only on the condition that $L \ge 2$) and $\Delta > 0$, then, for low values of n_0 , the stationary solution becomes

$$n_3 = K_3 \Delta / B \Delta_1 = D / B D_1 \tag{9}$$

and
$$w \simeq K_1 n_1 = \frac{K_3^2 \Delta A_2}{\Delta_1^2 B} = \frac{K_1 K_2 K_3 D}{B D_1}$$
 (10)

For $\Delta_1 \leq 0$ and $\Delta > 0$, the solution becomes nonstationary. A bicyclic system differs from a monocyclic one in this feature and its physical meaning is that, if $\Delta_1 \leq 0$, the chain $n_1 - n_2 - n_1$ (i.e., a chain consisting of two links) leads to an infinitely high reaction rate, if all the centers n_3 perish, so that the quadratic rupture does not play any rôle in the process.⁵

If the conditions of §2, especially (11) and (13), are satisfied, we may put, in scheme (III), $dn_1/dt = dn_2/dt = 0$ and reduce it to the equation

$$\frac{dn_3}{dt} = \frac{n_0 A_2}{\Delta_1} + K_3 \frac{\Delta}{\Delta_1} n_3 - B n_3^2, \qquad (IV)$$

having the same dependence upon the time as (II).

If the stationary reaction rate $w = K_3^2 \Delta A_2 / \Delta_1^2 B$ becomes very considerable already at $\Delta_1 \simeq +1$, then the term Bn_3^2 can be neglected as it was in the monocyclic scheme. However, if the stationary reaction rate is low (this, as already mentioned, will be the case only for slowly developing reactions) then the bicyclic scheme leads to new results, namely that the condition for the transition to a nonstationary régime is no longer $\Delta = 0$, but $\Delta_1 = 0$. This would mean that, in the case of a very pronounced rupture, the condition for inflammation is $\beta - \delta = 0$ for the first cycle $(n_1 - n_2 - n_1)$; while the second cycle, owing to the marked quadratic rupture, ceases to further the development of the reaction.

The above fact is of interest for any question relating to the nature of the explosion accompanying the oxidation of methane, hydrogen sulphide or arsine; as has been shown by Norrish in England and, in our Institute, by Shantarovitch, Jakovlev and Emanuel, these are typical cases of chain reactions with quadratic rupture developing slowly with time.⁶

In all these cases the oxidation proceeds slowly, the velocity first increasing according to the law

 $(e^{\phi t}-1)$ and then (when 10-20 percent has been consumed) attaining a constant value, after which it slowly decreases owing to lack of combustibles. Lowering the pressure or diminishing the diameter of the containing vessel leads to conditions where Δ becomes less than 0. Owing to the low value of n_0 , the reaction then practically ceases, as has been shown by Norrish for methane, by Spence for acetylene and, very clearly, by Shantarovitch for arsine. The increase of the temperature or the pressure is followed by a gradual acceleration until explosion sets in. The experimental evidence thus far available, points to thermal causes of the explosion (heating due to the normal temperature coefficient of the stationary reaction). However, in some cases, this cause may be sought in the acceleration caused by the decrease of Δ_1 to zero, or to be exact to almost zero. According to this explanation the explosion bears an essentially chain character. Such is the opinion of Bernard Lewis.

It must be noted that the above mechanism requires the condition that $L \gg 2$ and that at least one of the values of A be greater than unity. If L=1, and at least one A > 1, then Δ_1 cannot be zero; if all the coefficients A = 1 (i.e., in the absence of linear rupture), then Δ_1 is always equal to zero (even if L=1) and the stationary régime becomes impossible. In a recent paper Jost and Müffling⁷ give a scheme for hydrogen oxidation where the transition from a finite stationary reaction rate to an infinite one does not require linear ruptures and can proceed with a quadratic rupture alone. As far as I am aware, this idea is quite new, but it has no physical meaning in the case of the rapidly proceeding low temperature inflammation of hydrogen.8

This is easily understood. It suffices to modify the scheme slightly, assuming that, upon the reaction of the center n_1 , the centers n_2 and n_3 do

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⁸ The case will be different if, in addition to the quadratic rupture Bn_{3^2} , ruptures of the type Cn_{1^2} and Cn_{2^2} must also be considered.

 ⁶ R. G. W. Norrish and S. G. Foord, Proc. Roy. Soc.
 A157, 503 (1936); P. S. Shantarovitch, Acta Phisicochim.
 U.S.S.R. 7, 417 (1937); N. Semenoff, Acta Phisicochim.
 9, 453 (1938).

⁷ W. Jost and L. v. Müfflng, Zeits. f. physik. Chemie 183, 43 (1938).

⁸ Other statements appear to be open to criticism as for instance the statement that the determinant of a complex linear chain reaction scheme cannot be represented in the form of the difference $\beta - \delta$ (δ being the probability of branching and β that of the chain being broken), or the statement that my fundamental conceptions are contradicted by the presence in the denominator of the expression for the raction rate in schemes with a quadratic rupture of the square of $|\beta - \delta|$. Furthermore, the authors are examining a homogeneous system, where all the n_0 values are equal to zero and they do not consider the physical complications occasioned by neglecting n_0 .

not appear simultaneously, either one or the other being produced at a time.⁹

In the system of Eqs. (III), the term K_1n_1 in the second equation will be multiplied by the fraction $a=K_{11}/K_1$, and by the fraction $b=K_{12}/K_1$ in the third equation, where K_1 $=K_{11}+K_{12}$ (the sum of the reaction rates characterizing one or the other alternatives). The sum of a and b is equal to unity.

In the diagrams of the schemes these alternatives are shown by dotted lines (the place of the quadratic branching being marked by a cross X). Fig. 13 represents the scheme for L=2. Here it is obvious that the reaction of the center n_1 along the second cycle will be equivalent to a linear rupture with respect to the first cycle. And, therefore, in the case of a strong pronounced quadratic rupture which reduces the action of the second cycle to nothing, the stationary reaction will take place even for $A_1=A_2=A_3=1$, and then the transition from a stationary to a nonstationary régime becomes possible.

In this case the determinant

$$\Delta = \begin{vmatrix} -1 & 2 & 1 \\ a & -1 & 0 \\ b & 0 & -1 \end{vmatrix} = b + 2a - 1 = a$$

and the determinant

$$\Delta_1 = \begin{vmatrix} -1 & 2 \\ a & -1 \end{vmatrix} = 1 - 2a$$

Whence, from (9) and (10)

$$n_{3} = \frac{K_{3}\Delta}{B\Delta_{1}} = \frac{K_{3}a}{B(1-2a)} = \frac{K_{3}K_{11}}{B(K_{12}-K_{11})},$$

$$K_{1}n_{1} = \frac{K_{3}^{2}\Delta}{\Delta_{1}^{2}B} = \frac{K_{3}^{2}a}{B(1-a)} = \frac{K_{3}^{2}K_{1}K_{11}}{B(K_{12}-K_{11})^{2}},$$

$$K_{2}n_{2} = \frac{K_{3}^{2}K_{11}^{2}}{B(K_{12}-K_{11})^{2}},$$

i.e,

$$w \simeq R/(K_{12}-K_{11})^2$$

Upon a change of the temperature or the pressure, 1-La becomes either greater or less than 1, and thus, for $L \ge 1$, the transition from a sta-



FIGS. 13 and 14.

tionary to a nonstationary régime becomes possible in the absence of linear ruptures. The physical meaning of the above is clear only in the case of a very low stationary reaction rate, i.e., when K_{3}^{2}/B is small, which, as has already been pointed out, is hardly the case in the oxidation of hydrogen.

In conclusion let us reproduce Jost's scheme determined by the following chemical equations:

1.
$$OH+H_2=H_2O+H$$
,
2. $H+O_2=OH+O$,
3. $H_2+O=OH+H$,
4. $H+O_2+M=HO_2+M$,
5. $2HO_2=H_2O_2+O_2$,
6. $HO_2+H_2=H_2O_2+H$,
7. $H_2O_2+H=H_2O+OH$.

It may be noticed that the last equation is not at all characteristic of the scheme; the same results can be obtained without it, assuming that the H₂O₂ transforms into H₂O according, for instance, to the reaction $2H_2O_2 = 2H_2O + O_2$. The system of the first six reactions is shown by the diagram of Fig. 14 representing a polycyclic system consisting of a group of linear cycles and of one cycle possessing an alternative bond and containing a quadratic rupture. This system does not differ in principle from the case examined. Indeed, if we write down the determinant Δ together with the determinant Δ_1 of the group of linear cycles, then, with the aid of (9) and (10), we obtain the concentration of the active centers and the reaction rate. The results are of course similar to those obtained by Jost, except that in place of K_4 we get $(K_4 + K_2)$, since Jost did not take into account the water produced in the first reaction. If I take the liberty of reproducing these results, it is because expressions (9) and (10), as well as the diagram of the scheme, allow of a more concrete interpretation of the physical meaning of the relations to which schemes of this kind are leading.

⁹ Thus, in the reaction $O+H_2=OH+H$, the centers OH and H occur simultaneously. On the other hand, in the reactions $H+O_2+H_2=H_2O+OH$ and $H+O_2+M=HO_2$ +M, either the center OH or the center HO₂ arises.

§ 4. Mutual Promoting Action of the Chains. Quadratic Branching

Out of the great number of cases of this kind, we shall examine only one, where the development of the fundamental chain is due to two active centers and the resulting intermediate product n_3 perishes in two different ways: either reacting at a reaction rate K_4n_3 up to a certain final product (perishing without having contributed towards the development of the fundamental chain), or reacting up to another final product the reaction rate being proportional to the square of n_3 ($K_3n_3^2$), and producing at the same time an active center of the fundamental chain. We shall assume that $K_3n_3 \ll K_4$ and it is obvious that, throughout the reaction, n_3 cannot become greater than N, the number of molecules of the combustible in the initial mixture.

To illustrate this case let us examine the scheme for the oxidation of carbon disulphide:

1.
$$CS+O_2 = COS+O$$

2. $O+CS_2 = CS+SO$ fundamental chain.
1' $CS+CS_2+O_2 = (CS)_2+SO_2$
2' $O+O_2+M = O_3+M$
1" $CS+wall$
2" $O+wall$
3. $SO+SO=SO_2+S$; $S+CS_2=S_2+CS$
(quadratic branching).

4. $SO + O_2 = SO_3^*$; $SO_3^* + O_2 + CS_2 = 2SO_2 + COS$ (destruction of the intermediate product).

The spontaneous production of the active centers is due to the extremely slow reaction $CS_2+O_2=CS+SO_2$. The resulting COS can be gradually oxidized in an independent way according to the scheme

 $COS + O_2 = CO + SO_2.^{10}$

The constants K_1 , K_2 , K_3 , K_1' etc. are functions of the molecular concentrations of the reactant gases. In the case of the above scheme the corresponding relations are $K_1 = \kappa_1(O_2)$; $K_2 = \kappa_2(CS_2)$; $K_3 = \kappa_3$; $K_4 = \kappa_4(O_2)$, $K_1' = \mu(CS_2)(O_2)$; $K_2' = \mu_2(O_2)(M)$.

When the probability ϵ is close to unity, that the active center will perish on striking the wall, then K_1'' and K_2'' are of the same order as D_0/d^2p , while in the case of very low values of ϵ , they will be of the same order as $\epsilon u/4d$. In these relations d is the diameter of the containing vessel, *u* the velocity of the center due to thermal motion, D_0 the coefficient of diffusion at p=1mm, p the total pressure, $\kappa_{1, 2, 3, 4}$ the constants of the bimolecular, and $\mu_{1,2}$ that of the trimolecular reaction. If the development of the fundamental chain, its branching and the destruction of the intermediate products proceed by bimolecular reactions, and the rupture of the chains in the volume proceed by a trimolecular reaction, then, irrespective of the chemical mechanism of the process, we may assume that K_1 , K_2 and K_4 are proportional to p, and that K_1' and K_2' are proportional to p^2 , K_3 being independent of the pressure. With regard to K_1'' and $K_{2}^{\prime\prime}$, they may be assumed either to be independent of, or inversely proportional to p(according to the particular value of ϵ).

The corresponding equations have the form

$$dn_1/dt = n_0 - A_1 K_1 n_1 + L K_2 n_2 + K_3 n_3^2$$

$$dn_2/dt = K_1 n_1 - A_2 K_2 n_2,$$

$$dn_3/dt = K_2 n_2 - K_4 n_3 - K_3 n_3^2,$$

where

$$A_1 = \frac{K_1 + K_1' + K_1''}{K_1}; \quad A_2 = \frac{K_2' + K_2' + K_2''}{K_2},$$

the determinant of the fundamental chain being $\Delta_1 = A_1A_2 - L$; let us denote by Δ , the quantity $1 + L - A_1A_2$.

In all cases concerned, Δ and Δ_1 are >0. If $\Delta_1 \leq 0$, we are dealing with a nonstationary reaction, even in the absence of quadratic branching.

Let us first examine the stationary solutions. We have

$$K_1 n_1 = n_0 + K_3 n_3^2 / (\Delta_1 / A_2) \tag{1}$$

$$n_3 = \frac{n_0}{K_4 \Delta_1} \cdot \frac{2}{1 \pm (1 - \rho)^{\frac{1}{2}}},\tag{2}$$

and

¹⁰ Professor Kondratiew of our Institute, when studying the cold-flame oxidation of CS₂ by the method of absorption spectra, showed that large amounts of CS radicals and SO molecules are formed in the course of reaction. The amount of CS radicals exceeds by many times the equilibrium concentration at the given temperature. The CS radicals possess a lifetime of several minutes at room temperature and do not react noticeably with the oxygen. The latter fact gives rise to some doubt as to whether the CS radicals can be centers of the fundamental chain. This will be clear only after the examination of their interaction with oxygen at temperatures of the order of 100° C. The final products consist of CO, SO₂ and a considerable amount of COS. Kondratiew's paper has just gone to press.

where

$$\rho = \frac{4n_0 K_3 \Delta}{K_4^2 \Delta_1^2} \tag{3}$$

For low values of n_0 , the value of ρ is equally low. For very low values of n_0 , one of the two roots is

$$(n_3)_1 = n_0/K_4\Delta_1,$$
 (4)

the corresponding reaction rate (proportional to K_1n_1 or to K_4n_3) being n_0/Δ_1 . This solution does not differ from that which would be obtained in the absence of quadratic branching. This is the required root. The second root

$$(n_3)_2 = \Delta_1 K_4 / K_3 \Delta, \tag{5}$$

having an entirely different physical meaning, will be discussed later.

Thus, in order to obtain a stationary solution, in (2) the sign + should be taken. Upon the decrease of Δ_1 , or the increase of n_0 , the value of ρ increases, until it can be no longer neglected in (2). In this case the concentrations n_1 , n_2 and n_3 and the corresponding reaction rates K_1n_1 and K_4n_3 do not increase in the same proportion as n_0 (at a given Δ_1) but more rapidly. This appears to be the case in the photochemical reaction $H_2 + Cl_2$, with intense illumination (Kokotschaschwili). Recent and more detailed unpublished investigations of Lavrov and coworkers (Leningrad) show that since the increase of the reaction rate with the light intensity I(in the case of intense illumination) is greater than that required by the law of proportionality, the reaction cannot be explained by the heating of the mixture and in fact it takes place even under isothermal conditions. There is some reason to believe that we are dealing here with a mutual promoting action of the chains.¹¹

Upon a further increase of ρ , at the expense of the increase of n_0 or of the increase of temperature, resulting in a decrease of Δ_1 , a value greater than 1 can be obtained. The expression under the radical sign in (2) acquires an imaginary

to the scheme
$$HCl^*+Cl_2=H-Cl$$
. A branching Cl

process of the following form can be imagined to proceed upon collision of the two not very stable HCl_3 molecules: $HCl_3+HCl_3=2$ $HCl_2+Cl_2+Cl+Cl$.

value, a stationary solution being impossible. From $\rho=1$ upwards, the reaction accelerates with time. In the absence of quadratic branching, the condition for the transition to a nonstationary régime (the condition for inflammation) would be

$$\Delta_1 = 0. \tag{6}$$

If the rupture proceeds in the volume and on the surface according to the above scheme, condition (6) would determine the "peninsula of inflammation" with its upper and lower limits. In the case of a reaction of a linear type, the boundaries of this region are independent of n_0 .

Now, if a quadratic branching must also be accounted for, the condition (6) can be replaced by another, namely, $\rho = 1$ which according to (3) becomes

$$\Delta_1 = (4n_0 K_3 \Delta)^{\frac{1}{2}} / K_4. \tag{7}$$

This means that the inflammation proceeds more readily (i.e., the temperature of the inflammation falls) and further that the boundaries of the region of inflammation become dependent on n_0 ; the peninsula of inflammation shifts towards lower temperatures, if the number of initial centers is increased by some artificial means (illumination). The latter effect is characteristic of the mutual promoting action of the chains but it must be convincingly proved that the effect is not due to a heating of the gas. Experimental evidence appears to show that such is the case for a low temperature reaction of hydrogen inflammation.

At the limit of inflammation, i.e., for $\rho = 1$, we have according to (2)

$$n_3^* = 2n_0/K_4\Delta_1$$
 and $(K_1n_1^*) \simeq w^* = Cn_0/\Delta_1$, (8)

where C is of the order of 2.

Thus, in the case of quadratic branching, the maximum value of the stationary concentration and that of the reaction rate only twice exceed the corresponding values characterizing the same process at the same temperature in the absence of quadratic branching. In the latter case, for a great number of oxidation processes of the type of chain reactions, the reaction rate $n_0/\Delta_1 = n_0/(\beta - \delta)$ rises very slowly with the temperature, and only close to the self-inflammation limit (where $\beta - \delta$ approaches 0), does this increase become rapid. For these simple linear

¹¹ It can be assumed that the mechanism of quadratic branching is connected with a reaction between chlorine and the HCl* molecule which is extremely rich in energy and is formed in the reaction $H+Cl_2=HCl*+Cl$ according Cl

schemes the quantum yield, equal to $1/\Delta_1$, is low over the whole range of temperatures, except those which are close to the region of selfinflammation. In the case of quadratic branching, for high values of n_0 , the region of self-inflammation shifts considerably towards lower temperatures, while the reaction rate and the quantum yield on the boundary of the new region are almost the same as in the absence of quadratic branching, i.e., very low. This is characteristic of this type of reaction.



The same characteristic features are displayed by hydrogen-oxygen mixtures near the region of low-temperature inflammation, as has first been shown by Dubovitzky¹² and later by Nalbandjan of our Institute. At the very boundary, the length of the chain ν_{i} equal to half of the quantum yield, does not exceed 10. Fig. 15 gives some of the curves obtained by Nalbandjan showing the variation of the quantum yield with the temperature up to the region of inflammation (which depends on n_0). Curve 1 refers to the maximum illumination (in arbitrary units i), curve 2 to a twice fainter illumination, and curve 3 corresponds to experiments where the degree of illumination was 7 times less.13, 14

¹² F. I. Dubovitzky, Acta Phisicochim. U.S.S.R. 2, 761 (1935).

¹³ It is no easy matter to image a scheme for the reaction H_2+O_2 which would account for quadratic branching. One of the possible solutions is:

1. $H+O_2=OH+O$; 2. $O+H_2=OH+H$; 1. $H+O_2=OH+O$; 2. $O+H_2=OH+H$; 1. $H+O_2+M+HO_2+M$; 2'. $O+O_2+M=O_3+M$ or $O+H_2+M=H_2O+M$; 1". H+wall; 2". O=wall; 3. $OH+OH=HO_2+H$; 3'. $OH+H_2=H_2O+H$;

4.
$$OH + O_2 + H_2 = H_2O + HO_2$$
.

Satisfying certain conditions similar to those of §2 especially (11), but in which K_3 is substituted by K_3n_3 , the scheme (1) can be solved approximately, putting $dn_1/dt = dn_2/dt = 0$, whence

$$K_{1}n_{1} = \frac{n_{0} + K_{3}n_{3}^{2}}{\Delta_{1}/A_{2}}; \quad K_{2}n_{2} = \frac{K_{1}n_{1}}{A_{2}},$$

$$\frac{dn_{3}}{dt} = \frac{n_{0}}{\Delta_{1}} - K_{4}n_{3} + \frac{\Delta}{\Delta_{1}}K_{3}n_{3}^{2} = a - bn_{3} + cn_{3}^{2}.$$
(9)

In the case of a nonstationary solution, i.e., when $\rho = 4ac/b^2 > 1$

$$n_2 = 2a/\left[\sqrt{q} \cot\left(\sqrt{q/2}\right)t + b\right]$$

where $q = 4ac - b^2 > 0$ (10)

and the reaction rate

$$K_1 n_1 \sim K_3 n_3^2$$
.

According to expression (10) the reaction proceeds at first more slowly with a prolonged induction period and afterwards much more rapidly than would follow from the $e^{\phi t}$ law characteristic of a chain reaction with linear branching.

The oxidation of hydrocarbons in the coldflame region bears a similar kinetic character, which has led Professor Neumann (of our Institute) and co-workers¹⁵ to suppose that here also we have to deal with a quadratic branching of chains and has led him to give this hypothesis a chemical interpretation. He was also able to show that the addition of small amounts of peroxides brings down the temperature at which the cold flame appears, the effect being the more pronounced, the greater the amount of peroxide added. This would be in accord with the theory of mutual action, since the peroxides are playing the rôle of the active intermediate product.

The difficulty is that the reaction rate for (3') must be assumed of the same order as for (3), if not of a still lower order. The HO₂ molecules can perish on the walls. At high pressures (above the upper limit) the reaction $HO_2 + H_2O$ $=H_2O_2+OH$ can become noticeable; the latter scheme together with (4) might explain the chain of slow hydrogen oxidation at high pressures. As has been shown by N. Chirkov (reference 14).

¹⁴ N. Chirkov, Acta Phisicochim. U.S.S.R. 6, 915 (1937). This reaction proceeds at a rate proportional to (H₂O), so that, in the absence of water, it will be very slow. It is strange that the other workers who tried to find a mechanism for the slow oxidation of hydrogen have overlooked this circumstance.

¹⁵ M. B. Neumann and co-workers, Acta Phisicochim. U.S.S.R. 4, 575 (1936); 6, 279 (1937); 9, 861 (1938); 9, 827 (1938).



A direct proof in favor of the theory of mutual action has been obtained by Voronkov, Popilsky and myself in the oxidation of carbon disulphide.

Let us examine Eq. (9) and the physical meaning of the second root of $(n_3)_2$ in expression (5). The variation of dn_3/dt with n_3 for increasing ρ can be illustrated by curves similar to those in Fig. 16. Curve I corresponds to $\rho < 1$ or $b^2 > 4ac$, curve 2 to $\rho = 1$ or $b^2 = 4ac$, curve 3 to $\rho > 1$ or $b^2 < 4ac$. Stationary solutions are obtained only for $\rho < 1$. The points of intersection yield the two roots: $(n_3)_1$ and $(n_3)_2 = b/c$. The first of these roots is stable, the second being unstable. Indeed, if an instantaneous concentration n_3 be produced just slightly less than $(n_3)_2$, the concentration will continue to decrease automatically until it falls to $(n_3)_1$. A concentration slightly above $(n_3)_2$ will automatically grow to infinity, so that a nonstationary state will be obtained, though b^2 is still greater than 4*ac*. The physical meaning is that inflammation will set in if the experiment is conducted far from the temperature of selfinflammation, when $b^2 > 4ac$ and $\rho < 1$, when the stationary concentration is established and the reaction rate becomes practically zero, and if the instantaneous concentration n_3 of the intermediate product is brought artificially to a value equal or greater than $(n_3)_2 = b/c$.

Accordingly, a mixture of carbon disulphide and air was introduced into a long tube, one end being heated to a temperature sufficient for self-inflammation, while the remaining part of the tube was maintained at a much lower constant temperature. In the presence of mutual promoting action, the flame produced in the hot part will propagate along the cold part of the

tube at the expense of the mutual action of the intermediate products which diffuse from the flame zone, attaining in the unburnt gas a concentration equal to $n_3 \ge (n_3)_2 = b/c$. Since we used poor mixtures $(0.03 \text{ percent } CS_2)$ which, even in the case of adiabatic combustion, are able to raise the temperature by no more than some 15°, we had to deal with the influence of the possible heating of the mixture, and thus prove the isothermal nature of the propagation of the flame. It was shown that, under the above conditions, the flame travels at a constant rate, its temperature being lower by 100° than that required for the self-inflammation of the mixture in the same tube. Fig. 17 shows (1) the region of selfinflammation and (2) the region of the flame expanding in an air mixture (0.03 percent of CS_2) in a glass tube 20 mm in diameter.

Because of considerable mathematical difficulties, I did not succeed in developing an exact theory of the propagation of the flame through diffusion of the active product responsible for the quadratic branching. I therefore made use of an expression given by Frank-Kamenetzky of our Institute for the diffusional propagation of the flame when the quadratic autocatalysis is caused, not by the intermediate, but by the





final product. It would be easy to show that this expression can be used as an approximate solution of the problem at hand. According to this expression, the rate at which the flame travels is

$$w = \left(\frac{fD}{2}\right)^{\frac{1}{2}} \left(1 - \frac{b}{f}\right),\tag{11}$$

where, as before $b = K_4$ and

$$f = c(\mathrm{CS})_0 = \frac{K_3 \Delta(\mathrm{CS}_2)_0}{\Delta_1}.$$

 $D=D_0/p$, the coefficient of the diffusion of the centers is inversely proportional to the total pressure p. $(CS_2)_0$ is the number of CS_2 molecules in the initial mixture. $\Delta = 1+L-A_1A_2$ and $\Delta_1=A_1A_2-1$. Assuming that the rupture of the chain takes place only at the first link (i.e., $A_2=1$), which means that the oxygen atom begins to react as soon as $K_2+K_2'+K_2''/K_2\sim 1$ and that L=1, we have $\Delta = 2-A_1$ and $\Delta_1=A_1-1$;

$$\frac{\Delta}{\Delta_1} = \frac{2 - (K_1 + K_1' + K_1'')/K_1}{(K_1 + K_1' + K_1'')/K_1 - 1} = \frac{K_1 - K_1' - K_1''}{K_1 + K_1''}$$

On the assumption that the fundamental chains are sufficiently long $(K_1 \gg K_1' + K_1'')$, we obtain

$$f = K_1 K_3 (CS_2)_0 / (K_1' + K_2''); \qquad (13)$$

considering the relation between the coefficients K and $(CS_2)_0$ and the pressure, and putting $\epsilon \ll 1$, we obtain

$$f = Ap^2/(cp^2 + B),$$
 (13')

where A, C and B depend on the temperature, being independent of the pressure, and

$$b = K_4 = g \not p. \tag{14}$$

The limits of the flame propagation are determined from (11) and the condition f=2b or, substituting (13) into (14), from the equation

$$gcp^2 - Ap + Bg = 0, \tag{15}$$

which determines the boundaries of the peninsulashaped region in which the flame expands, considering that g, c A and B depend on the temperature according to a law of the type $e^{-E/RT}$. At some distance from the end-point of the peninsula, the upper and the lower limits of propagation are determined from the expressions

$$p_1 = \frac{2gB}{A}$$
 and $p_2 \frac{A}{2gc}$ (16)

or

 $p_1 = Pe^{+E/RT} \quad \text{and} \quad p_2 Qe^{-E/RT}. \tag{17}$

The experimental data for the upper limit fit extremely well into (17), as may be seen from Fig. 18 where the averaged experimental values are shown by circles. It will be easy to express the rate of propagation of the flame in any point inside the peninsula by the limits of propagation.

Since $D = D_0/p$, where D_0 depends on the temperature and since g depends on the temperature as $\sqrt{Te^{-E/RT}}$, we obtain

$$w = \left(\frac{fD}{2}\right)^{\frac{1}{2}} \left(1 - \frac{f}{b}\right)$$
$$= K_0 \frac{T}{T_0} e^{-E/RT} \frac{1 - p/p_2 - p_1/p}{(p_1/p + p/p_2)^{\frac{1}{2}}}.$$
 (18)

According to experimental evidence, $E \simeq 0$ and b depends on the partial pressure (O₂) in a mixture of oxygen and nitrogen, $K_0 = K_0'(O_2/p)$. For $T_0 = 410^{\circ}$ K, K'_{410} has been found equal to 56, whence

$$w = 56 \frac{(O_2)}{p} \frac{T}{410} \frac{1 - p/p_2 - p_1/p}{(p_1/p + p/p_2)^{\frac{1}{2}}}$$

The above expression shows the influence of the pressure and that of the temperature on the propagation of the flame, the first in an explicit form, the other through the limits p_1 and p_2 .

It must be noted that the theoretical expressions (11) and (19), similar to those for the velocity of thermal propagation of the flame, do not conform to experiment; indeed, at the limit of propagation, the velocity has a finite value, while theoretically it should be zero. In the case of the thermal theory, this discrepancy is due to the fact that no account has been taken of the heat transfer to the walls; in our case it is due to the special simplifications which had to be made when using the expression given by Frank-Kamenetzky. All the values of the limits p_1 and p_2 for (19) must therefore be found by extrapolating to zero-velocity the experimental curves showing the relationship between w and p. This operation does not present any difficulties in the case of the upper limit, the extrapolated values exceeding by some 10 percent the corresponding experimental values. In the case of the lower limit, the



steepness of the curves renders the extrapolation doubtful, and p_1 is usually calculated from (19) from the maximum of the w-p curves and the experimental value of p_2 . The values of p_1 thus calculated have been found to fit quite well into (17), allowing the computation of P and E.

With the aid of the 5 constants Q, E_2 , P, E_1 and K_{410} it becomes possible to calculate the



absolute values of the boundaries of the inflammation peninsula, as well as the velocities of the propagation of the flame, for any p and Tinside the region of the flame expansion for mixtures with a 0.03-percent content of carbon disulphide with varying amount of oxygen and nitrogen. The two curves of Figs. 19 and 20 illustrate the good agreement between the experimental values of the velocity (marked by black circles) and those calculated (marked by white circles); one refers to a mixture of 50 percent O_2+50 percent $N_2+0.03$ percent CS_2 at $T=134^\circ$, the other to the same mixture at $T=216^\circ$ C; the quantity v/K is plotted on the abscissae. K in the first case is 28, in the second K_1 it is 33.5.

In the case of carbon disulphide, the theory is thus seen to be supported by experimental evidence, both from a qualitative and a quantitative point of view.¹⁶

¹⁶ In this brief note I must refrain from examining some extremely interesting and not yet fully explained phenomena concerning the lack of reproducibility; in some particular tubes (in no way different from others), the projecting part of the peninsula of inflammation appears as if it had been cut by a vertical line, which means that, at low temperatures, the flame does not expand. For higher temperatures, the upper and the lower limits, as well as the reaction rate, show the same numerical values as in normal tubes. Sometimes, a hitherto normal tube suddenly becomes erratic.