

KINETICS OF CHAIN REACTIONS

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The study of a considerable variety of homogeneous gaseous reactions has revealed that their kinetics can be interpreted on the basis of a theory advanced already in main outline by Arrhenius. According to this theory only the so-called activated molecules can enter into reaction. The number of these molecules is a function of temperature and of the gaseous concentrations and therefore the reaction velocity is also a function of these parameters. The number of activated molecules may sometimes change very rapidly with temperature (when the "activation energy" is very large) and concentration but this change remains always steady and continuous and so should the reaction velocity.

Still, a large number of reactions are known, the rate of which, although homogeneous, shows a peculiar discontinuous dependence on the outside parameters. To this type of reactions belong, for instance, the phenomena of explosions and inflammations, in which the rate changes from, occasionally, immeasurably small values to exceedingly large ones as the result of only negligibly small changes in the parameters—the temperature and the pressure of the reaction body.

An opinion exists that such behavior is not in disagreement with the activation theory of Arrhenius. Namely, the heat evolved in the rather slow initial stages of a reaction must heat up somewhat the reaction mixture. This results in an acceleration of the reaction velocity owing to its high temperature coefficient. If the conditions are such that, at all times, the heat losses by the gas mixture to the outside are less than the heat supplied by the

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reaction, the warming up and therefore the reaction velocity will be auto-accelerated ad infinitum (or until the reaction is over) and this phenomenon constitutes an explosion. As the writer has previously shown (1), such interpretation of the explosion mechanism leads to the conclusion that, for each composition and total pressure of the reacting mixture, there exists a certain critical temperature below which an explosion is impossible and above which an explosion will occur. The critical temperature is dependent on the pressure of the explosive mixture and for each critical temperature there exists a critical pressure above which an explosion occurs and below which only a slow, sometimes a very slow, reaction takes place. The relation between the critical pressure and the critical temperature is expressed by the equation

$$\log p = \frac{A}{T} + B \quad (1)$$

where the constant A is dependent on the energy of activation only, whereas the constant B depends on the composition of the reaction mixture and on the conditions of the heat conductance from the reacting gases. Testing this relation experimentally Sagulin (2), has found it confirmed in a considerable number of explosive gaseous mixtures.

Nevertheless there exists very strong evidence indicating that such a theory of "thermal" explosions is incorrect in the majority of cases and that therefore an interpretation of the explosion phenomena by means of the classical concepts of chemical kinetics (the theory of Arrhenius) is, generally speaking, impossible.

First of all, there are a number of explosive reactions in which the temperature of the flame is quite low, sometimes hardly exceeding room temperature. Of this type are, for instance, the burning of ether and of carbon bisulfide in oxygen, but, particularly striking is this type of reaction exhibited in the oxidations of the vapors of phosphorus and of sulfur at low pressures.

Furthermore, there are a number of explosive reactions in which the critical pressure is independent of the temperature. Of this type are oxidations of phosphorus and of carbon monoxide. From the point of view of the theory of thermal explosions

indicated above, such behavior is possible only when the constant A (equation 1) is equal to zero and this means that the energy of activation is also equal to zero. But if $E = 0$, these reactions should be extremely rapid even when there is no inflammation. Instead, if phosphorus vapor is mixed with such amounts of oxygen that no inflammation occurs, the oxidation velocity, as has been shown by the writer (3), is extremely slow, no measurable reaction occurring for many hours. Similarly, a carbon monoxide-oxygen mixture, explosive at temperatures above a certain critical temperature, practically does not react at all if the temperature is maintained at only a few degrees below the critical value.

All such observations disagree with the assumption that the energy of activation of these reactions is equal to zero. The theory of thermal reactions thus is incapable of accounting for some of the experimental evidence. But it is not only the phenomenon of incandescence which indicates the insufficiency of the classical concepts of chemical kinetics. It is well known that frequently immeasurably small amounts of foreign substances influence radically the rate of chemical reactions. Perhaps the most striking effect of this type is the action of water vapor, discovered by Dixon and by Baker. Thus, for instance, sufficiently dried phosphorus and oxygen do not react at all; the photochemical formation of hydrogen chloride in visible light is stopped completely according to Coehn when the partial pressure of water vapor is less than 10^{-3} mm., but goes with normal velocity when this pressure exceeds 10^{-4} mm.

Polanyi (4) has shown that the dark formation of hydrogen chloride goes very rapidly if hydrogen contains traces of sodium vapor. Riabinin and the writer (5) succeeded in demonstrating that sulfur vapor in oxygen does not ignite at all at temperatures from 50 to 100°. However, a presence of infinitesimal traces of ozone in oxygen is sufficient to cause rapid combustion. Thus, the reaction either does not go at all or proceeds with a very high velocity depending only on whether there are traces of ozone present in the reaction vessel. Hinshelwood and Simpson (6) and earlier Dixon have found that small amounts of nitric oxide

decrease by 200° the explosion temperature of the hydrogen-oxygen mixture. A similar observation has been made by Sagulin and the writer (7) in the case of carbon monoxide-oxygen mixtures where the explosion temperature is decreased by 50° even when nitric oxide, being first admitted into an empty reaction vessel, is pumped out by a high vacuum pump before the reaction mixture is introduced. Under these circumstances the partial pressure of NO should not exceed 10^{-5} mm. Not less striking is the effect of negative catalysts or inhibitors. As has been shown in detail by Bäckström (8) the homogeneous rate of oxidation of aldehydes is reduced manyfold on addition of 0.01 per cent and less of certain inhibitors. Oxygen exercises a similar action on the photochemical formation of hydrogen chloride according to observations of Bodenstein. Different authors have demonstrated that addition of vapors of organometallic compounds increases the explosion temperature of hydrocarbons, thus inhibits the explosion.

All these and many other facts relating to homogeneous catalysis can hardly be reconciled with the classical theory of chemical kinetics.

A GENERAL THEORY OF CHAIN REACTIONS

Already at the first glance one weak point in the classical theory of chemical reactions becomes quite obvious. According to this theory, activated molecules are formed as the result of collisions of molecules whose relative kinetic energy exceeds the energy of activation E . Let us call n the number of activated molecules thus formed per unit time. Assuming that most of these activated molecules react before they are somehow de-activated, the rate of reaction, according to the theory of Arrhenius, is equal to n . The number n is calculated usually thus. The total number of molecular collisions per unit time is Z ; the activation occurs only when the relative energy of colliding molecules is larger than E ; the probability of this is $e^{-E/RT}$. Thus, according to the classical theory the number of reacting molecules is given by the equation

$$w = n = Z e^{-E/RT} \quad (2)$$

Such conclusion however is incorrect as has been pointed out already by Christiansen and Kramers. Indeed, each elementary reaction act is accompanied by an accumulation of energy equal to $E + Q$, where Q is the heat of reaction. This energy is transformed ultimately into heat energy, i.e., is distributed as kinetic and potential energy among all molecules of the gas. In the time immediately following the reaction process, on the other hand, all this energy is distributed as potential and kinetic energy among only those few molecules which are produced in the elementary process of reaction.

Let us assume that each of the molecules resulting in the reaction carries a part φ of the total energy $E + Q$. An activation will then occur on collision of some other molecules with the reaction product when the available energy of this molecule exceeds the magnitude $E - \varphi$. The probability of this process is $e^{-\frac{(E - \varphi)}{RT}}$. Thus, each primary reaction can lead to the formation of secondary reaction processes, the probability of such action being $\alpha = a_0 e^{-\frac{(E - \varphi)}{RT}}$. It follows that the number of reacting molecules is expressed not by equation (2) but by:

$$w = n + \alpha w \quad (3)$$

which takes into account this secondary activation. Equation (3) leads to a general expression for the rate of reaction:

$$w = \frac{n}{1 - \alpha} \quad (3a)$$

When the magnitude α is equal to unity, each primary reaction process causes an infinite sequence of secondary reactions—an infinite reaction chain. And since the primary links of these chains (due to thermal activation) are produced to the number n per unit time, the total rate must be obviously infinite. This result is obtained also from equation (3a) when α is equal to unity. When α is less than unity the number of secondary links

produced by one primary reaction is finite and is equal to $\nu = \frac{1}{1 - \alpha}$. The quantity ν can be interpreted as the length of chain.

$$\nu = \frac{1}{1 - \alpha} = \frac{1}{\beta} \quad (4)$$

where by β is denoted the probability that the chain is stopped at any given link. It may happen also that α is larger than unity. This can occur for instance when the total energy $E + Q$ is larger than twice the activation energy E . Under these circumstances each primarily activated molecule may lead to the formation of two new activated molecules. When $\alpha > 1$, equation (3a) has no positive solution. A closer consideration of this case (1) has shown that, however small is n , the reaction velocity, once started, will increase auto-acceleratingly to infinity. The rate of increase is the more rapid, the larger is $\alpha - 1$. The chains are here not only infinitely long, but, besides, they branch out, causing new chains to be started independently of the primary activation.

Summarizing, the three possibilities: $\alpha < 1$; $\alpha = 1$; $\alpha > 1$; characterize the following processes: (1) $\alpha < 1$; the primary links in the chains are started by the primary activation. The length of each chain is finite. (2) $\alpha = 1$; the primary links on the chains are started by the primary activation. The chains are infinitely long. (3) $\alpha > 1$; the chains are infinite and are started not only by the primary but also by the secondary activation. They branch out and one primary activation starts not one but infinitely many infinitely long chains. This can be illustrated by figure 1.

The question may arise, in how far the new chemical kinetics here indicated satisfy the laws of thermodynamics. Assuming the reaction to be $A \rightleftharpoons B$ and the reaction velocities of both processes to be w_1 ($A \rightarrow B$) and w_2 ($B \rightarrow A$); instead of equation (3a), the equations (5) are obtained:

$$\begin{aligned} w_1 &= n_1 + \alpha_{11}w_1 + \alpha_{21}w_2 \\ w_2 &= n_2 + \alpha_{22}w_2 + \alpha_{12}w_1 \end{aligned} \quad (5)$$

Here n_1 and n_2 are the numbers of primarily activated and reacting molecules in the direct and in the reverse reaction. The coefficients α_{11} ; α_{22} ; α_{21} ; and α_{12} are defined in the following manner: α_{11} is the probability that a given primary process of the direct reaction results in the formation of a secondary process of the direct reaction; α_{22} is the same magnitude for the reverse reaction; α_{21} is the probability that a given elementary process of the reverse reaction leads to the formation of a reaction process of the direct reaction; α_{12} is the probability that a process of the direct reaction results in the formation of a process of the reverse reaction.

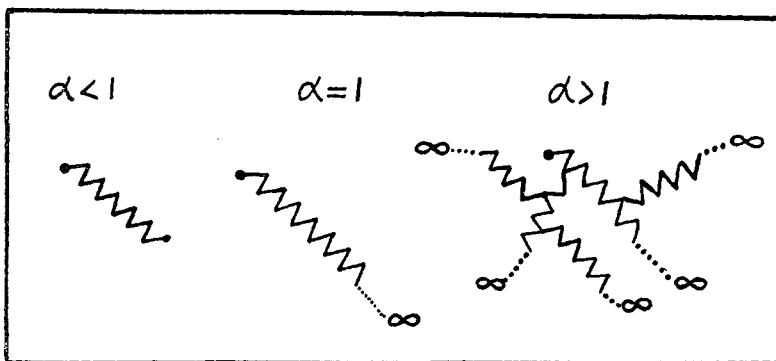


FIG. 1. THE REACTION CHAINS

Classical kinetics give $w_1 = n_1 = Z_1 e^{-E_1/RT}$ and $w_2 = n_2 = Z_2 e^{-E_2/RT}$ where E_1 and E_2 are the respective activation energies of the direct and of the reverse reaction.

Thermodynamics require that in the state of equilibrium the ratio of the velocities $\frac{w_2}{w_1}$ should be proportional, at least in the first approximation, to $e^{-Q/RT}$, where Q is the heat change accompanying the direct reaction $A \rightarrow B$. It follows therefore that

$$K = \frac{w_2}{w_1} = \frac{Z_2}{Z_1} e^{-\frac{E_2 - E_1}{RT}} = C e^{-Q/RT}; E_2 - E_1 = Q \quad (6)$$

Thus, to satisfy thermodynamics, it is necessary only to assume (as has been pointed out already by Arrhenius) that the difference in the energies of activation is equal to the heat of reaction. But, as will now be shown, the same condition is sufficient to reconcile also the new equations (5) with thermodynamics.

The energy produced in each process of the direct reaction is equal to $E_1 + Q$. On the average each of the molecules of the reaction products carries a part φ of this energy. It follows that

$$\alpha_{11} = C_1 e^{-\frac{E_1 - \varphi}{RT}}$$

and

$$\alpha_{12} = C_2 e^{-\frac{E_2 - \varphi}{RT}} \quad (7)$$

α_{11} indicating the probability that one of the reaction products collides with (and activates) a molecule A having an available thermal energy in excess of $E_1 - \varphi$ and α_{12} indicating the probability that the same reaction product collides with a molecule B having an energy in excess of $E_2 - \varphi$. When it is remembered that n_1 is proportional to the probability that a molecule having an energy in excess of E_1 collides with a molecule A and that n_2 is proportional to the probability that a molecule with energy E_2 collides with a molecule B, it will become evident that:

$$\frac{n_1}{n_2} = \frac{Z_1 e^{-E_1/RT}}{Z_2 e^{-E_2/RT}} = \frac{C_1 e^{-\frac{E_1 - \varphi}{RT}}}{C_2 e^{-\frac{E_2 - \varphi}{RT}}} = \frac{\alpha_{11}}{\alpha_{12}} \quad (a)$$

Similarly it follows that:

$$\frac{\alpha_{22}}{\alpha_{21}} = \frac{n_2}{n_1} \quad (b)$$

and, furthermore, the additional equation (c) can easily be derived:

$$\alpha_{11} \alpha_{22} = \alpha_{21} \alpha_{12} \quad (c)$$

Solving the system of equations (5) one obtains:

$$w_1 = \frac{n_1 (1 - \alpha_{22}) + \alpha_{21} n_2}{(1 - \alpha_{11}) (1 - \alpha_{22}) - \alpha_{12} \alpha_{21}}$$

$$w_2 = \frac{n_2 (1 - \alpha_{11}) + \alpha_{12} n_1}{(1 - \alpha_{11}) (1 - \alpha_{22}) - \alpha_{12} \alpha_{21}}$$

Making use of the equations (a), (b), (c) the following expressions are obtained:

$$w_1 = \frac{n_1}{1 - \alpha_{22} - \alpha_{11}} \tag{8}$$

$$w_2 = \frac{n_2}{1 - \alpha_{22} - \alpha_{11}}$$

Whence: $K = \frac{w_2}{w_1} = \frac{n_2}{n_1} = C e^{-Q/RT}$ in accordance with the law of equilibria. Van't Hoff, deducing from the thermodynamic equation (6), concluded that the rates w_1 and w_2 as functions of temperature must be represented by the expressions:

$$w_2 = C_2 e^{-E_2/RT} \quad \text{and} \quad w_1 = C_1 e^{-E_1/RT}; E_2 - E_1 = Q;$$

but, assuming more generally:

$$w_2 = \frac{C_2 e^{-E_2/RT}}{\psi(T)} \quad \text{and} \quad w_1 = \frac{C_1 e^{-E_1/RT}}{\psi(T)} \tag{9}$$

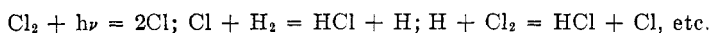
one still obtains expressions not in disagreement with the laws of equilibria, however fast may $\psi(T)$ change with T . Such more general type of temperature function for the rate of chemical reaction is the type which results from the application of the concepts of the chain theory. Consequently the Arrhenius-Van't Hoff equation:

$$\log w = -\frac{A}{T} + B$$

represents only a limiting case and can be approximately correct for those reactions only in which α is very close to zero or when it is independent of temperature.

THE FINITE CHAINS

The concept of reaction chains has been established as the result of a series of photochemical investigations. Thus, in the case of hydrogen chloride formation about 10^5 molecules of HCl are formed for one light energy quantum absorbed by chlorine. The length of chains is here therefore: $\nu = 10^5$, the probability that a chain is stopped at a given link $\beta = \frac{1}{\alpha} = 10^{-5}$ and the quantity $\alpha = 1 - \beta = 0.99999$. In all probability the chain is propagated in a way suggested by Nernst:



The secondary activation in this reaction consists in that, through the reaction of a chlorine atom with one hydrogen atom, the other atom of the hydrogen molecule is made free and becomes an active reaction center for the consecutive chain links. The above scheme corresponds, of course, to $\alpha = 1$, thus to infinite chains. The reason why the chains are finite in reality has been explained by Bodenstein and consists in a breaking off of the chains by oxygen molecules. According to Göhring (9) such action is due to the free atoms of chlorine and of hydrogen entering into reaction with oxygen and thus becoming incapable of continuing the chain. If one assumes that each collision of Cl or H with O_2 leads to reaction, the probability of stopping the chains will be expressed by

$$\beta = \frac{[\text{O}_2]}{[\text{Cl}_2]} + \frac{[\text{O}_2]}{[\text{H}_2]} \quad (10)$$

In a more general case this probability will be

$$\beta = k_1 \frac{[\text{O}_2]}{[\text{Cl}_2]} + k_2 \frac{[\text{O}_2]}{[\text{H}_2]}$$

and correspondingly the expression for the rate of reaction will be:

$$w = \frac{n}{\beta} = n \nu = \frac{n [\text{H}_2] [\text{Cl}_2]}{(k_1 [\text{H}_2] + k_2 [\text{Cl}_2]) [\text{O}_2]}$$

Considering that n — the number of primarily started chains — is proportional to the product of light intensity and concentration of chlorine (a case of weak absorption of light), the equation for the rate of reaction takes the form:

$$w = c \frac{I_0 [\text{Cl}_2]^2 [\text{H}_2]}{(k_1 [\text{H}_2] + k_2 [\text{Cl}_2]) [\text{O}_2]}$$

which is in complete accord with experimental data. One can estimate the inhibiting action of oxygen assuming $k_1 = k_2 = 1$. Since in this case:

$$\nu = \frac{1}{\beta} = \frac{1}{\frac{[\text{O}_2]}{[\text{H}_2]} + \frac{[\text{O}_2]}{[\text{Cl}_2]}}$$

the chains will be about 1000 molecules long if the ratios $[\text{O}_2]:[\text{H}_2]$ and $[\text{O}_2]:[\text{Cl}_2]$ are of the order of magnitude of 10^{-3} ; when these ratios are about 10^{-5} , the chains are 10^5 molecules long. Thus, a change in oxygen concentration from 0.1 to 0.001 per cent changes the chain length a hundred-fold. This shows how the presence of very small amounts of impurities can change the rate of chain reactions and indicates once more the nature of negative catalysis or inhibition which has been treated decisively already by Christiansen (10). A particularly convincing experimental confirmation of this theory of inhibition has been obtained by Bäckström (8), (11) in his work on oxidation of aldehydes and of sodium sulfite solutions.

Of a very similar nature is the inhibitive action of the solid walls of the containing vessel, first described by the author (3) for the oxidation of phosphorus vapor, observed also by Hinshelwood and Simpson (6) and by Pease (12) for the thermal reaction of oxygen and hydrogen, by Pease (12) for the thermal oxidation of some hydrocarbons and recently observed by Triffonoff of this laboratory (7) in the case of photochemical HCl formation at low pressures. Such action of the walls is due undoubtedly to adsorption and de-activation on the walls of activated molecules (atoms of chlorine and hydrogen in the hydrogen chloride reaction), an effect which is similar to the action of oxygen in the hydrogen chloride reaction for instance.

Assuming, as a first approximation, that the diameters of all molecules are equal and using the Einstein-Smoluchowski diffusion expression, the writer could show (7), that in the case that the chains are not broken off homogeneously, i.e., in the gas mixture itself, the length of chains ν_0 , as determined by the inhibitive action of the walls, is given by:

$$\nu_0 = \frac{6 \pi x^2}{4 \lambda_0} [\text{H}_2] [\text{Cl}_2] \quad (11)$$

Here x is the distance from the origin of the chain to the wall and λ_0 the mean free path at unit total pressure. Calculating the magnitude of ν_0 at atmospheric pressure and for ordinary dimensions of the reaction vessel, one obtains values of the order of $\nu_0 = 10^9$. This figure, being considerably in excess of the experimentally determined length of chains in the HCl reaction, indicates that at such pressures the chains are broken off almost exclusively by action of oxygen in the gas mixture itself and the action of the walls is quite unimportant. However, when the pressure is decreasing, the chains will be more and more frequently stopped on the walls since ν_0 decreases as the square of the pressure, whereas the inhibition in the gas space remains constant, provided the relative concentration of oxygen is constant.

At sufficiently low pressures the length of the chains is fully determined by (11) and since the average value of x is proportional to the linear dimensions of the vessel (diameter in case of cylindrical vessels), a proportionality of the reaction velocity to the square of the dimensions of the vessel must be expected. This last inference from the theory has been fully confirmed by Triffonoff (7). Hinshelwood and Simpson (6) succeeded in showing that at temperatures near the explosion point, where the homogeneous rate predominates, the rate of water formation is much faster in an empty vessel than in a vessel filled with pieces of broken porcelain. Furthermore, according to these writers, additions of helium, argon or nitrogen accelerate the reaction velocity. This observation is also fully in accord with the theory of inhibition by the walls: neutral gas, by decreasing the mean

free path, decreases the diffusion to the walls and thereby increases ν_0 — the length of chains — and thus the total rate. The writer has compared the influence of inert gases found experimentally in the work of Hinshelwood and Simpson with the magnitude of the influence to be expected theoretically and has arrived at very good agreement.²

The action of homogeneous catalysts in chain reactions is exemplified particularly clearly in the experiments of Polanyi, mentioned previously, in which it was shown that chlorine and hydrogen react in the dark at low temperatures if hydrogen is first passed over molten sodium and carries with it traces of sodium vapor. Polanyi has given a complete interpretation of this effect by employing the chain theory. He has shown earlier that the reaction of chlorine with sodium vapor goes according to the scheme $\text{Cl}_2 + \text{Na} = \text{NaCl} + \text{Cl}$. Thus, a free chlorine atom is formed in each elementary process and this then starts, in the hydrogen-chlorine mixture, the usual Nernst-chain, the result being that for each reacted sodium atom hundreds and even thousands of HCl molecules are formed.

The function of a positive catalyst is thus to create artificially the initial links of the chains, when these cannot be formed by the thermal activation energy alone.

It is at least probable that the catalytic action of water vapor is similar in nature. Water molecules, either owing to their large electric moment or to some other as yet unidentified property, must be able to facilitate the formation of the initial chain links—the reaction centers—, the thermal energy alone being unable under the circumstances to achieve this result.

These suggestions do not exclude the possibility that the action of some of the known catalysts may be due to a selective destruction of inhibitors, which prevent otherwise the normal course of a reaction.

² Using, as before, the Einstein-Smoluchowski expression and assuming all molecular diameters to be equal, the equation (11) can be generalized to:

$$\nu_0 = \frac{6\pi \times 2}{4\lambda_0^2} [\text{H}_2] [\text{Cl}_2] \left(1 + \frac{[\text{A}]}{[\text{H}_2] + [\text{Cl}_2]} \right) \quad (12)$$

Here [A] denotes the partial pressure of the inert gas. The expression can be used, suitably modified, for the present reaction also.

THE INFINITE CHAINS

The velocity of a reaction $w = \frac{n}{1 - \alpha}$ becomes infinite when α exceeds unity. The magnitude of α which is a function of temperature and of the concentrations of the reacting gases, changes

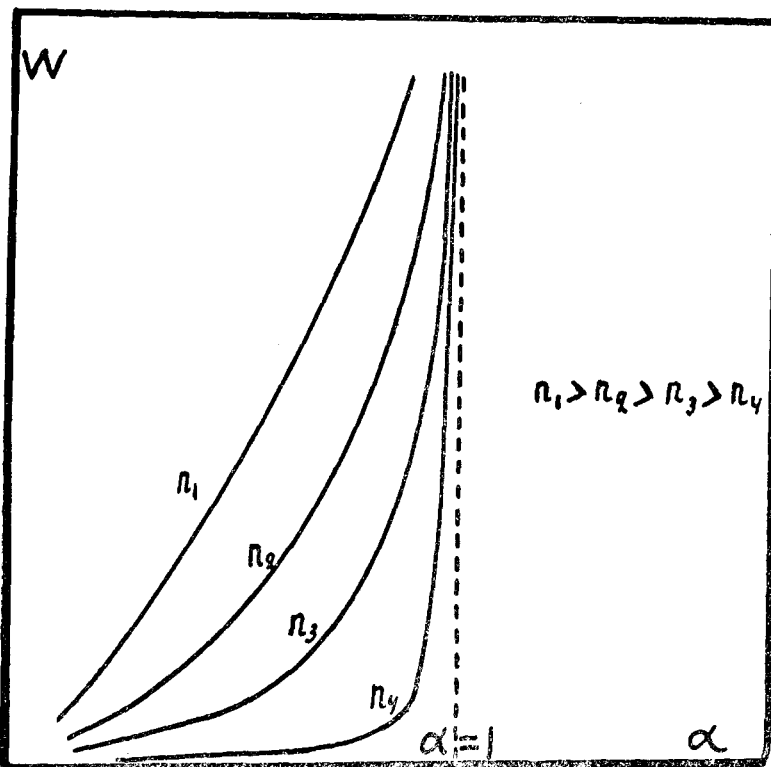
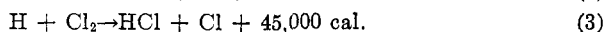
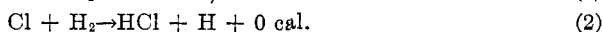


FIG. 2. REACTION VELOCITY AS A FUNCTION OF α AND n

with the change of these parameters and, being less than unity under some conditions, may exceed unity when the conditions are suitably altered. Plotting the rate of reaction as a function of α one obtains curves of the type presented in figure 2. They all yield $w = \infty$ when $\alpha = 1$. The smaller is n , the more rapid is the change from the condition in which the rate is practically

zero to the condition of infinite velocity. Thus an idea can be formed of the critical region in which a reaction goes over into inflammation or explosion, since this latter means a reaction of extremely high velocity. One can say that all chemical reactions in which α exceeds unity are inflammations or explosions and that the condition $\alpha = 1$ determines the region where a normal reaction becomes auto-accelerating or explosive. It becomes important to investigate how α can exceed unity in concrete cases. Let us consider, for example, the hydrogen-chlorine reaction again, which, as it is well known, can become explosive under suitable conditions.

The mechanism of this reaction has been discussed before:



At first glance the impression may be gained that here α can be either less or equal to unity but never more. That this is not so, the following consideration indicates. Reaction (3) is accompanied by an energy evolution of 45,000 cal. per mol. This energy must be distributed between the two resulting particles HCl and Cl. Let us assume that one of these carries the larger portion of this energy equal to φ . If this activated molecule collides with a chlorine molecule having itself 56,000- φ cal. energy, two new chlorine atoms will be formed, and thus two new chains originated. The probability of this process is

$$C e^{-56000-\varphi/RT} = C e^{-U/RT}$$

The coefficient C in this expression is of the order of unity and may be a function of the partial pressures of hydrogen and of chlorine.³

³ For instance, if it is assumed that the energy φ is lost on every collision with molecules of hydrogen or with molecules of chlorine having energy less than U , the quantity C is expressed by:

$$C = 2 \frac{[\text{Cl}_2]}{[\text{H}_2] + [\text{Cl}_2]}$$

If this energy is not lost on collisions with hydrogen but only on collisions with chlorine having energy less than U , the coefficient is:

Not considering the possibility of this secondary formation of chlorine atoms we would have the expression $\alpha_0 = 1 - \beta_0$, where β_0 stands for the probability of a given chain being broken. Taking the secondary atom formation with the probability $e^{-U/RT}$ into account, an expression for α is obtained which can be written thus:

$$\alpha = 1 - \beta_0 + C e^{-U/RT} \quad (13)^4$$

Expression (13) is less than unity at low temperatures but must become larger than unity at some temperature T_k . From this we may conclude that T_k is the critical temperature of explosion for a given hydrogen-chlorine mixture. Thus the condition for occurrence of explosion can be written:

$$\beta_0 = C e^{-U/RT} \quad (14)$$

Considering that the coefficient C for a given composition of the gas is independent of the total pressure, whereas the magnitude β_0 is probably proportional to some negative power of it,⁵ the

$$C = 2$$

If this energy, even on collisions with chlorine, is lost only on every n th collision, the coefficient is:

$$C = 2n$$

It should be pointed out furthermore that for a given composition of the gas the coefficient C is independent of the total pressure, even if the first of the above assumptions is the correct one.

⁴ To avoid misunderstanding it is appropriate to point out why earlier in this article we defined the probability of a chain being broken as equal to $\beta = 1 - \alpha$, whereas now the expression (13) is derived. This is due to the circumstance that β_0 of equation (13), is, according to its definition, the probability of a chain being broken without reference to a possible branching off. The true magnitude of β —the probability of a complete disappearance of a chain with all its branching, is:

$$\beta = \beta_0 - C e^{-U/RT}$$

⁵ When all the chains are broken off on the walls β_0 is: (cf.) equation (11)

$$\beta_0 = \frac{1}{\nu_0} = \frac{K_1}{[H_2][Cl_2]} = K p^{-2}$$

On the other hand when all the chains are ended in the gas phase by oxygen alone, β_0 is (compt. equation (10)):

$$\beta_0 = [O_2] \left(\frac{1}{[H_2]} + \frac{1}{[Cl_2]} \right) = K p^0$$

equation (14) can be written:

$$K p^{-n} = C e^{-U/RT}$$

or:

$$\log p = \frac{U}{n RT} + B = \frac{A}{T} + B$$

This is a relation which was found experimentally by Sagulin (2) to hold for a large variety of explosive gaseous mixtures. As was pointed out in the beginning of this article, this expression was derived theoretically for the "thermal" explosions, that is for explosions occurring according to the classical views on chemical kinetics. The above shows in addition that a chain explosion also may yield the same relation between critical pressure and temperature. It must be pointed out in addition that the chain theory does not exclude that a "thermal" explosion may not precede the chain explosion, since autoacceleration caused by superheating may occur when α is still less than unity. Accordingly other characteristics of the explosions must usually be adduced in order to decide whether an explosion is of the chain- or of the thermal-type. The explosions of carbon disulfide-oxygen mixtures, for instance, which give a linear relationship between $\log p$ and $\frac{1}{T}$ with an angle of inclination indicating large

A , are undoubtedly chain explosions since the flame is quite cold and is very sensitive to the presence of traces of impurities. There are sufficient grounds for assuming also that the explosions of saturated hydrocarbons with oxygen are similarly chain explosions. In agreement with this, for instance, is their known sensitivity to various "antiknocks" present even in minute quantities. The nature of the explosions of $H_2 + Cl_2$ or of Cl_2O , on the other hand, is somewhat uncertain at present, although, in the opinion of the writer, here also we are hardly dealing with straight thermal explosions.

The chain explosion type is most clearly represented in the

reactions of phosphorus and sulfur vapors and of carbon monoxide with oxygen and these will now be considered here in some detail, being the basis of the explosion theory here developed.

INFLAMMATIONS OF PHOSPHORUS, SULFUR, AND CARBON MONOXIDE

It has been known for a long time that phosphorus vapor undergoes rapid combustion only when the oxygen pressure is maintained within certain limits. Jorissen (13), in particular, has considered the limiting pressures as the critical explosion limits and has investigated more in detail the upper critical oxygen pressure. The question of the lower limit of the oxygen pressure was, however, scarcely investigated until the writer and his collaborators became interested in this phenomenon. The researches resulted in discovery and investigation of several somewhat unusual characteristics of the—as it was named—residual pressure. When oxygen is slowly admitted through a capillary into an evacuated vessel in which some white phosphorus is present, the pressure increase during an initial time interval manifests the absence of any reaction. When the oxygen pressure reaches a certain value p_r , a sudden visible inflammation occurs and thereafter phosphorus vapor continues to burn. During this period no pressure increase can be observed which indicates that all newly admitted oxygen is immediately consumed in the reaction. The walls of the vessel become gradually covered by a non-transparent layer consisting probably of P_2O_5 and of red phosphorus. When the further flow of oxygen is interrupted the luminous reaction is instantaneously extinguished, whereby the pressure remains equal to the critical value p_r . This last feature of the process was the one which suggested the name residual-pressure for the critical pressure p_r . That the remaining gas is oxygen is evident for instance from the observation that this gas is not condensed in liquid air. The residual oxygen may be in contact with phosphorus for many hours without any reaction taking place. This has been established not only by the constancy of the residual pressure but also by the observation that when the flow of oxygen into the vessel is resumed, inflammation takes place instantaneously, instead of

occurring, as was described before, only after a certain time. The existence of the residual pressure was demonstrated furthermore in the following way. A mixture of phosphorus vapor and oxygen at a pressure less than p_r is gradually compressed; only when the pressure reaches a perfectly definite value a sudden inflammation occurs.

The residual pressure of oxygen is a function of the size of the vessel and of the pressure of the phosphorus vapor. With saturated phosphorus vapor at room temperature and in vessels of a few cm. in diameter it is of the order of 10^{-2} mm. mercury. At the time of inflammation, as well as during the following combustion, the temperature of the gas mixture is raised only very little judging from the absence of any pressure increase.

Studying the laws governing the residual pressure, without however very great precision being achieved, the following results were obtained by the writer:

1. p_r is independent of the temperature of the vessel.
2. p_r is inversely proportional to some power n of the pressure p_{P_4} of phosphorus vapor; n is between 0.5 and 1.
3. p_r is inversely proportional to some power r of the diameter of the vessel; r is between 1.5 and 2.
4. p_r is decreased on diluting phosphorus vapor by argon.⁶ The relation between p_r and the pressure of argon p_A follows very closely the following expression:

$$p_r \left(1 + \frac{p_A}{p_r + p_A} \right) = \text{const.}$$

All these regularities can be united in a single equation (15):

$$p_r p_{P_4}^m d^n \left(1 + \frac{p_A}{p_r + p_A} \right) = \text{const.} \quad (15)$$

On the whole it is obvious that phosphorus vapor and oxygen will either not react at all or react with an extremely high velocity,

⁶ This last phenomenon is very distinct. One can take, for instance, a mixture of phosphorus vapor and oxygen below the p_r pressure and begin admitting argon into the vessel. At some definite pressure of this latter, inflammation occurs.

and the transition between these two states occurs within an unusually narrow interval in the values of the external parameters. Furthermore, that parameter which plays the main rôle in most of the explosions—the temperature—has no effect on this reaction.

In addition to the lower critical pressure of oxygen there exists also an upper critical pressure above which similarly no inflammation occurs. The phenomenon of this upper critical pressure has been described by several authors, who state that the value of the critical pressure is extremely sensitive to the presence of minute quantities of various substances. Quite recently a study of this phenomenon and an extension of the experiments on the lower critical pressure has been undertaken also in this laboratory (7).

The procedure was to admit oxygen into a vessel containing phosphorus and cooled by liquid air, then warm up the vessel to some definite temperature. If no inflammation occurred, oxygen was gradually pumped out through a capillary. At some pressure the inflammation occurred and went over usually into a violent burning of the phosphorus, followed frequently by destruction of the apparatus. The upper critical pressure of oxygen investigated from a few mm mercury to a pressure of nearly one atmosphere was found to be independent of temperature and to be directly proportional to the pressure of phosphorus vapor. The value of p_{\max} , which it attains with phosphorus vapor saturated at room temperature, is near to 600 mm. Thus, the relation between critical phosphorus and the upper oxygen pressure is:

$$\frac{p_{P_4}}{p_{\max}} = \text{const.} \quad (15a)$$

which means that when the percentage concentration of phosphorus decreases below a certain value, no inflammation can occur. A relation of this type is known to hold for almost all explosive mixtures, and it has frequently been observed that the presence of foreign substances can influence the value of the critical percentage concentration.

Extending earlier experiments of the writer on the residual pressure of oxygen to lower vapor pressures of phosphorus, Kowalsky was able to show that the equations of the upper and of the lower critical pressure of oxygen are nothing but the two limiting cases of the same general relation determining the explosion conditions of the phosphorus-oxygen mixtures. A

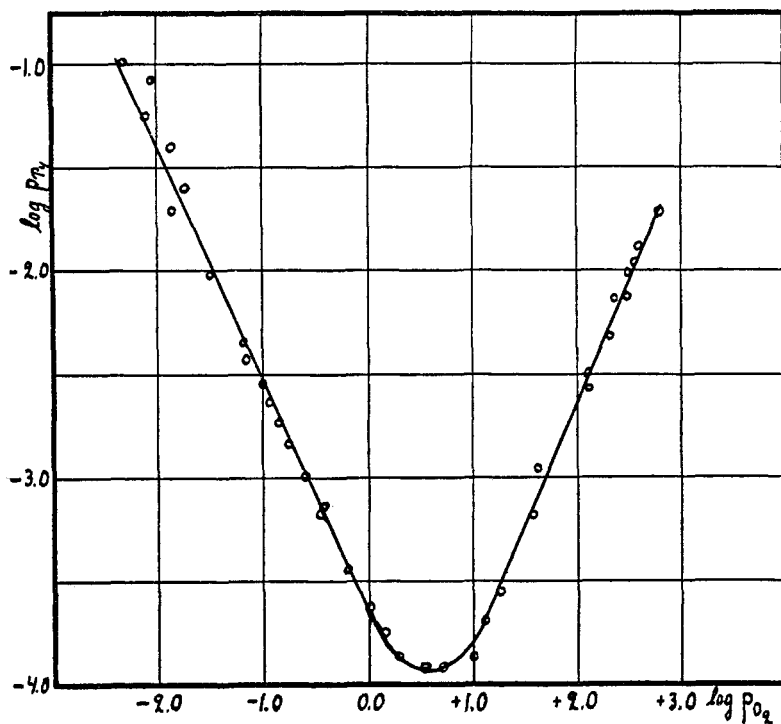


FIG. 3. INFLAMMATION LIMITS FOR $P_4 + O_2$ MIXTURES

transition region was found in which both curves flow smoothly together. These and our earlier experiments are represented on figure 3 in which the abscissae are the logarithms of the oxygen and ordinatae the logarithms of the phosphorus pressures (both in mm. mercury) and the region above the curve ABC is the explosion range.

When a comparison is made between the usual diagram of the

explosion pressure as a function of composition (fig. 4) and the laws governing the combustion of phosphorus, a very great similarity is found.⁷ The only difference is that the total critical explosion pressure in the middle section of the curve is now very small (of the order of 10^{-2} mm) and that the region CB (in figure 4, B represents oxygen concentration, A that of phosphorus), limited by the straight line C, according to the equation

$$\frac{P_{P_4}}{P_{O_2 \max}} = \text{const.},$$

is very narrow.

Conversely we may conclude that the phenomenon of the minimum or maximum critical pressure of one of the components is a peculiar property of all explosive mixtures and that therefore its theoretical interpretation is of far reaching importance. In this laboratory, besides phosphorus, the inflammation of sulfur (14) has also been investigated. Here, similarly, the existence of a minimum as well as a maximum pressure of oxygen has been observed. It was found furthermore that sulfur vapor can be burned in oxygen at temperatures even considerably below 100° . Therefore, the statement, frequently found in text-books, that the inflammation temperature of sulfur is 285° , is somewhat misleading. This temperature is significant only in that respect that the vapor pressure of sulfur reaches here a value for which the upper critical pressure of oxygen becomes equal to one atmosphere. At pressures below atmospheric the combustion can go at much lower temperatures. However, below 100° no spontaneous inflammation usually occurs, even with pressures within the explosion interval. But, as was mentioned previously, immeasurably small traces of ozone cause inflammation in this temperature range.

Sagulin (2) and also Garner and Gomm (15) have found that mixtures of carbon monoxide and oxygen explode at a minimal

⁷ The law of the residual pressure $p_1 p_2^m = \text{const.}$ can be written thus:

$$p^I + m = \frac{\text{const.}}{\gamma (1 - \gamma)^m}.$$

where p is the total pressure, $p_1 = \gamma p$ and $p_2 = (1 - \gamma) p$.

pressure p_{\min} of the order of a few centimeters and that this pressure increases very slowly from 20 to 30 mm. when the temperature is decreased from 736 to 578°. However, there exists a critical temperature T_k below which at no pressure does an explosion occur. Sagulin and the writer have recently studied

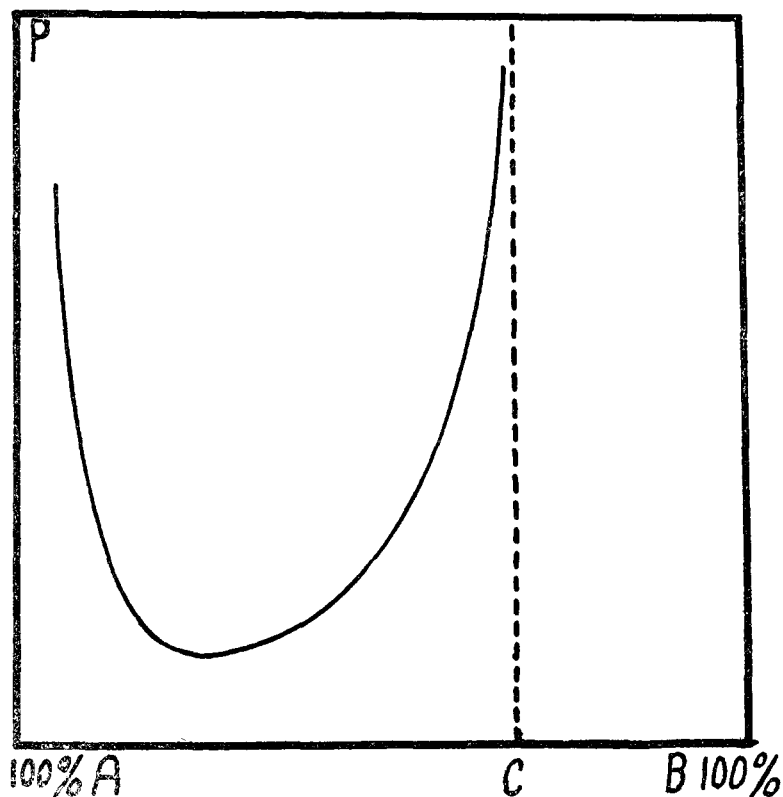


FIG. 4. EXPLOSION PRESSURE AS A FUNCTION OF COMPOSITION

more in detail the significance of this critical temperature. It was found that above the critical temperature an explosion occurs only within certain limits of the pressure of the mixture—from a p_{\min} to a well defined p_{\max} . The composition of the mixture has very little influence on these pressures. The relation experimen-

tally obtained between the critical pressure and the temperature is indicated on figure 5. The explosion is possible only within the area bounded by the curve ABC. The value of p_{\max} varies with temperature, changing from 60 mm. at 570° to 380 mm. at 683° . A sufficient further increase of the pressure should change this explosion finally, as can be deduced theoretically, into a thermal

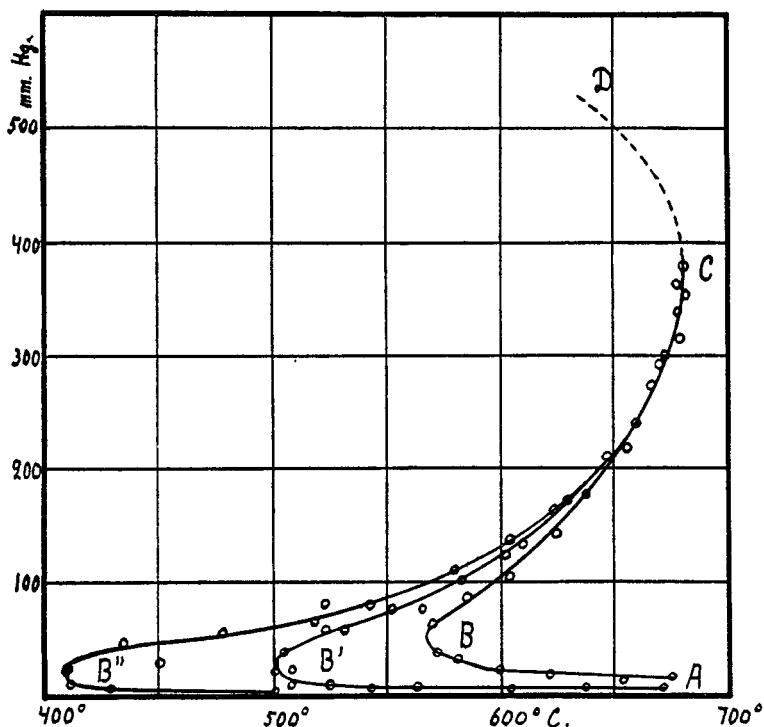


FIG. 5. EXPLOSION PRESSURE-TEMPERATURE RELATION FOR CO + O₂ MIXTURES

explosion. The critical pressure of this latter is indicated on figure 5 by the dotted line, CD following from the equation (1)

$$\log p = \frac{A}{T} + MB,$$
 with a large A, thus with a very high heat of activation, which is more than probable for the carbon monoxide-oxygen reaction. If this suggestion is correct, the complete

region of explosion is bounded by the curve ABCD. It is remarkable that an addition of even immeasurably small amounts of NO ($\sim 10^{-5}$ mm.) extends the explosion region to considerably lower temperatures, increasing the upper and decreasing the lower critical pressure as shown by the curve AB'C of figure 5.

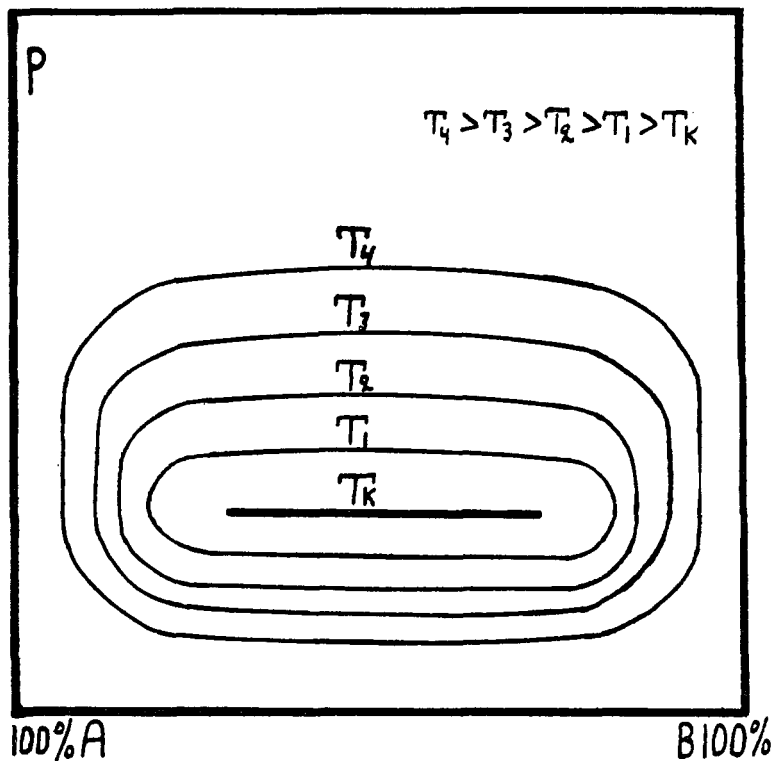


FIG. 6. EXPLOSION PRESSURE AS A FUNCTION OF COMPOSITION FOR CO + O₂ MIXTURES

Measurable quantities of NO (0.5 to 1.0 mm.) decrease the limiting T_k by almost 200° (the curve AB'C on figure 5.). The measurement of p_{\max} has been carried out by us in the following manner: 1. On introducing the carbon monoxide-oxygen mixture at a pressure larger than p_{\min} and at a temperature lower than

T_k , the vessel is slowly warmed up.⁸ At some temperature T_1 , an explosion occurs, and this temperature was found to be the higher, the higher was the pressure of the reacting mixture.

2. After warming up the vessel to some temperature $T > T_k$, it is rapidly filled by the gas mixture to a pressure $p > p_{max}$; the inflammation which starts when the pressure becomes larger than p_{min} is extinguished when $p > p_{max}$. Afterwards the gas mixture is passed slowly through the vessel and the pressure is gradually reduced. At some pressure an explosion occurs and this pressure is the desired p_{max} .

Both these methods gave results in good agreement.

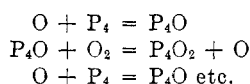
It should be pointed out here that the effect of the maximum total explosion-pressure of the carbon monoxide-oxygen mixtures and the existence of the maximal partial pressure of oxygen in phosphorus combustion, are quite different phenomena. Representing the data for $CO + O_2$ reactions in a diagram of the same type as figure 4, one obtains figure 6, in which the explosion region is enclosed by the curves drawn for the successively increasing temperatures $T_k < T_1 < T_2$ etc.

Considering the theory of the phenomena described one must remember that the reaction velocity $w = \frac{n}{1 - \alpha}$ becomes infinite when $\alpha = 1$. Nevertheless, in the case of sulfur vapor, even when the condition $\alpha > 1$ is fulfilled, an inflammation occurs only when traces of ozone are introduced. The only reasonable explanation of this last effect is the following: the reaction is started by oxygen atoms, which, at these temperatures, cannot be formed spontaneously (that is by thermal activation) on account of the very large energy of dissociation of O_2 involved. Therefore $n = 0$. But when $n = 0$, no matter how large α is, the reaction cannot develop. It suffices however to introduce artificial reaction centers (the dissociation $O_3 = O_2 + O$ for instance requires much less energy than $O_2 = 2O$.) to obtain a finite n , even though it may be small. Once the reaction is started and $\alpha > 1$, the

⁸ The thermal reaction below the explosion point is very slow.

rate will be autocatalytically accelerated, until an inflammation occurs.

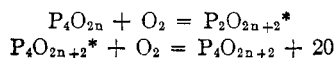
In the case of the burning of phosphorus vapor the reaction centers are formed spontaneously. It is nevertheless likely that in this reaction as well, the reaction centers are oxygen atoms. The difference in behavior in comparison with sulfur may be attributed to a very slow but probable reaction with solid phosphorus in which oxygen atoms are produced. The mechanism of the gaseous reaction can be written thus:



Assuming that the chains are broken on the walls, the probability of breaking a chain is $\beta_0 = \frac{1}{\nu_0}$ where ν_0 is given by (12)

$$\nu_0 = \frac{6 \pi d^2}{4 \lambda_0^3} [\text{P}_4] [\text{O}_2] \left(1 + \frac{[\text{A}]}{[\text{P}_4] + [\text{O}_2]} \right) \quad (16)$$

The mechanism of the phosphorus reaction suggested above includes only the main chain. But there is a possibility of the chains branching owing to the consecutive reactions of P_4O_2 to form finally P_4O_{10} :



The asterisk indicates here an excess internal energy. The second of the reactions can occur only when the kinetic energy of the oxygen molecules O_2 , together with the excess energy φ_{Δ}^* of the $\text{P}_4\text{O}_{2n+2}$ molecule, exceeds 160,000 cal. Denoting the difference $160,000 - \varphi = U$ we find that the probability of this secondary activation is $e^{-U/RT}$ and according to the equation (14) the condition of inflammation is expressed by $\beta_0 - 2 e^{-U/RT} = 0$, therefore:

$$\nu_0 = \frac{6 \pi d^2}{4 \lambda_0^3} [\text{P}_4] [\text{O}_2] \left(1 + \frac{[\text{A}]}{[\text{P}_4] + [\text{O}_2]} \right) = \frac{1}{2} e^{+U/RT} \quad (16a)$$

or, at a constant temperature:

$$d^2 [P_4] [O_2] \left(1 + \frac{[A]}{[P_4] + [O_2]} \right) = \text{constant} \quad (16b)$$

This is the same expression as one obtained experimentally (equation 15, p_r of equation (15) is now expressed as $[O_2]$). Even

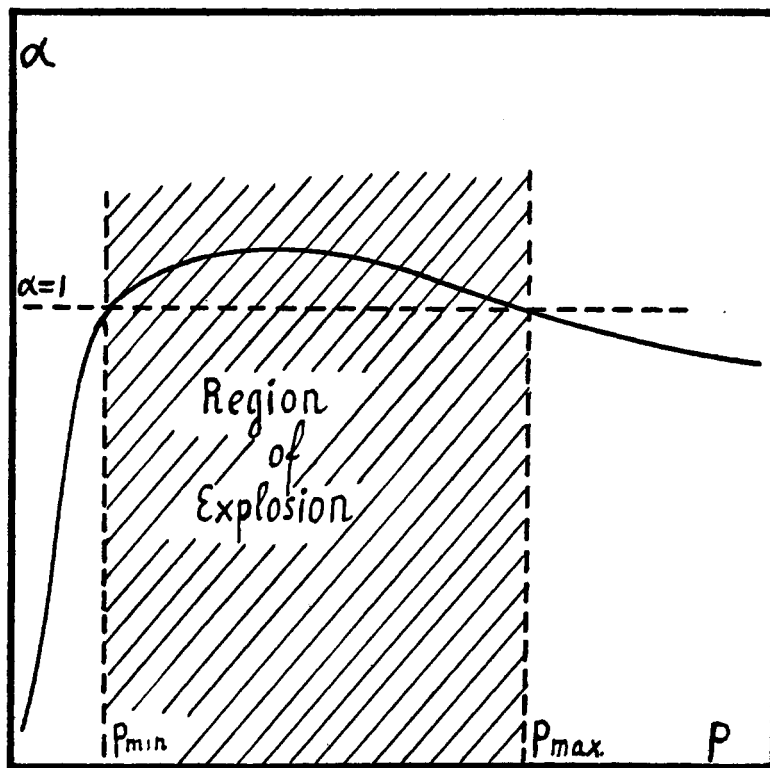


FIG. 7. α AS A FUNCTION OF PRESSURE

more, the theory enables one to compare the theoretical residual pressure with the experimentally determined value. The experiments have shown that p_r is independent of temperature. Taking into account the probable error of this determination it can be shown that the magnitude $e^{-U/RT}$ of equation (16a) does not exceed 0.1 at room temperature. The magnitude of λ_0 is known,

so that from equation (16b) the theoretical residual pressure ($[O_2]$ or p_r) can be easily calculated. Values thus obtained agree within a factor of two with the experimentally determined values.⁹ Going over now to the phenomenon of the maximal critical pressure one is forced unfortunately to concede that at present the

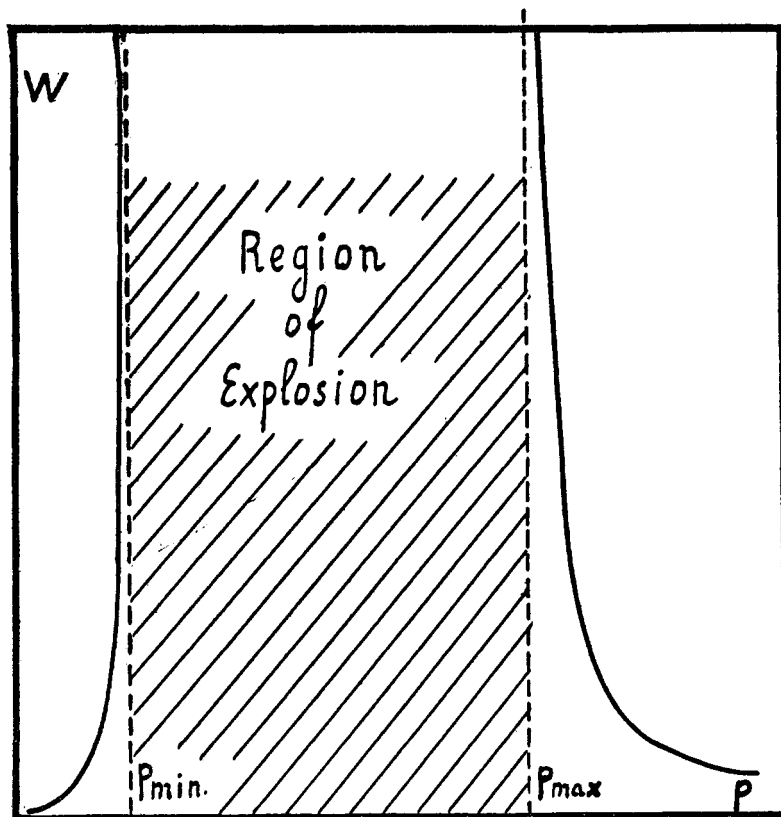


FIG. 8. REACTION RATE AS A FUNCTION OF PRESSURE

theory of this effect is not as certain. The chain theory, however, indicates at least a general direction along which the explanation should be sought. The magnitude of a , as a function of the partial pressure of oxygen, judging from experimental data in the

⁹ See the forthcoming article in *Z. physik. Chem., Abt. B.*

phosphorus reaction, has apparently the shape represented in figure 7; it has thus a maximum $\alpha > 1$ and cuts in two points the ordinate $\alpha = 1$. Assuming such a relation for α , the reaction rate as a function of oxygen pressure will be represented by figure 8.

Why α decreases again when the pressure of oxygen exceeds some value is difficult to answer definitely. It is possible, however, that oxygen contains some impurity reacting with oxygen atoms and thereby breaking the chains. The concentration of this impurity [R] must be proportional to the concentration of oxygen: $[R] = \mu [O_2]$, the coefficient μ being probably very small. In a case of this type the ordinary probability of breaking a chain must be increased by the probability of an oxygen atom reacting with the impurity and thus also ending the chain. Therefore, instead of the expression:

$$w = \frac{n}{1 - \alpha} = \frac{n}{\frac{1}{\nu_0} - e^{-U/kT}}$$

one obtains:

$$w = \frac{n}{\frac{1}{\nu_0} - e^{-U/RT} + \frac{\mu [O_2]}{\mu [O_2] + [P_4]}} \quad (17)$$

where $e^{-U/RT}$ is of the order of 0.1. When the pressure of oxygen is small, the third term of the denominator is very small also and can be therefore neglected. Thus the condition $\frac{1}{\nu_0} - 0.1 = 0$, still determines the minimal critical pressure of oxygen. For large oxygen pressures $\frac{1}{\nu_0}$ becomes negligibly small but instead $f = \frac{\mu [O_2]}{\mu [O_2] + [P_4]}$ grows. At some $[O_2]_{\max}$ when $f > 0.1$ the inflammation becomes impossible again. The condition determining the maximal oxygen pressure is therefore:

$$\frac{\mu [O_2]_{\max}}{\mu [O_2]_{\max} + [P_4]} = 0.1$$

from this follows:

$$[\text{O}_2]_{\max} = \frac{0 \cdot 1 [\text{P}_4]}{1 \cdot 1 \mu} \quad \text{or} \quad \frac{[\text{O}_2]_{\max}}{[\text{P}_4]} = \frac{0.09}{\mu} = \text{const.}$$

Thus the direct proportionality between $[\text{O}_2]_{\max}$ and $[\text{P}_4]$ in accordance with experimental results is obtained. The experimentally determined ratio of oxygen to phosphorus pressure was of the order of 10^4 , thus μ is of the order of 10^{-5} and the concentration of the assumed impurity in oxygen need not be larger than 0.001 per cent. In favor of this explanation of the maximal pressure is the observation frequently made that the maximal pressure is very sensitive to the presence of traces of foreign substances. Several observations of this character have been made in this laboratory also.

The reaction theory here presented accounts not only for the two limiting cases (chains stopped exclusively on the walls or exclusively in the gas phase) but, when considered more in detail, also for the transition region, in particular for the experimental observation (see figure 3) that a lower pressure of phosphorus vapor exists below which at no oxygen pressures an explosion occurs. To show this we rewrite now the condition of explosion (from 17)

$$\frac{I}{\nu_0} - e^{-U/RT} + \frac{\mu [\text{O}_2]}{\mu [\text{O}_2] + [\text{P}_4]} = 0, \quad (18)$$

using for ν_0 the value given by expression (16) in absence of an inert gas: $\nu_0 = \text{Cd}^2 [\text{P}_4] [\text{O}_2]$, substituting: $e^{-U/RT} = a$ and assuming $\mu [\text{O}_2] < [\text{P}_4]$, thus

$$\frac{I}{\text{Cd}^2 [\text{P}_4] [\text{O}_2]} - a + \frac{\mu [\text{O}_2]}{[\text{P}_4]} = 0, \quad (18a)$$

Introducing further $\frac{I}{\text{Cd}^2 a} = k_1$, and $\frac{\mu}{a} = k_2$ one obtains

$$k_2 [\text{O}_2]^2 - [\text{P}_4] [\text{O}_2] + k_1 = 0, \quad (18b)$$

an equation which yields as solutions:

$$[\text{O}_2]_{\min} = \frac{[\text{P}_4] - \sqrt{[\text{P}_4]^2 - 4 k_1 k_2}}{2 k_2} \quad (19)$$

$$[\text{O}_2]_{\max} = \frac{[\text{P}_4] + \sqrt{[\text{P}_4]^2 - 4 k_1 k_2}}{2 k_2} \quad (19a)$$

Equations (19) and (19a) give, for the condition: $[\text{P}_4]^2 > 4 k_1 k_2$ the experimentally obtained limiting expressions:

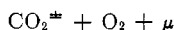
$$[\text{O}_2]_{\min} = \frac{k_1}{[\text{P}_4]} \quad \text{and} \quad [\text{O}_2]_{\max} = \frac{[\text{P}_4]}{k_2}$$

and show in addition that a critical phosphorus vapor pressure $[\text{P}_4]^2 = 4 k_1 k_2$ exists, below which the root becomes imaginary, thus an explosion becomes impossible at any oxygen pressures. It may be added that the simplification $\mu [\text{O}_2] <]\text{P}_4]$ made above in order to arrive to expressions (19) and (19a) does not change the conclusions reached here, although it simplifies very materially the calculations.

The existence of the maximal total pressure in the combustion of carbon monoxide is more difficult to interpret. The theory cannot be based upon the inhibiting action of some impurity because the expression $\frac{[\text{O}_2]}{[\text{O}_2] + [\text{CO}]}$ is independent of total pressure for a given composition of the gas. It is noteworthy that substitution of air instead of oxygen gives the same value for the maximal pressure p_{\max} of inflammation (by p_{\max} is meant here the total pressure $[\text{CO}] + [\text{O}_2] + [\text{N}_2]$). All this indicates rather some physical than chemical cause of the phenomenon. One might consider, for instance, the following reaction scheme:



(The occurrence of the second reaction requires approximately 10,000 calories additional activation energy of O_2). A triple collision of the type:



in contradistinction to reaction (2) may result in no formation of oxygen atoms, these recombining immediately and the energy being transferred to μ (this being some other, not further defined molecule). Such a mechanism gives the desired explanation but since no experimental evidence is available at present further discussion appears unjustified. The only conclusion that can be drawn is that a higher concentration of molecules facilitates somehow the breaking of the chains, the probability of this happening increasing with pressure. Such assumption will lead to a relationship between p and T of the same type as was obtained experimentally in the combustion of carbon monoxide.

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