Gas explosions and the theory of chain reactions*

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Explosions in general and gas explosions in particular are among the most interesting phenomena in nature. These phenomena most clearly manifest the passive forces of chemical resistance by which nature protects against the destructive action of the second law of thermodynamics. In them one can most clearly observe the boundary of chemical stability of a substance against the effects of temperature and pressure, i.e., the boundary at which the forces of passive resistance lose the ability to withstand the external influences and the substance almost instantaneously passes into the forms required by the second law.

Much as the boundary of mechanical stability is determined by the strengths of the forces acting between molecules prior to breaking (it is thus related to elastic and plastic deformation effects) and the boundary of electrical stability (breakdown of dielectrics) derives directly from an analysis of the electrical conductivity of insulators at voltages below the breakdown voltage, so must the boundary of chemical stability (explosion) be sought by studying the chemical transformations, often infinitely slow, that occur prior to the onset of the conditions necessary for explosion. No matter how slow the rates of these transformations are, they reflect the weakening of the forces of chemical resistance that will lead to explosion as the external influence becomes stronger. Thus the question of the nature of explosions and their causes is intimately related to the study of the kinetics of reactions that often begin long before the onset of conditions necessary for explosion.

This paper will be limited to a review of the latest developments in the theory of chain reactions, which will probably shed some light on the mechanism responsible for the ignition of gaseous mixtures.

The development of chemical kinetics can be divided into two main periods. The first of these was begun by the work of van't Hoff and Arrhenius at the end of the last century. This period culminated in the magnificent work of Hinshelwood in the field of bimolecular and monomolecular reactions. The results of this period can be summarized as follows: The only molecules that participate in a reaction are those whose energy (potential or kinetic), distributed according to the Maxwell–Boltzmann law, exceeds a certain characteristic value E, which is specific to each given reaction and is called the activation energy. In the case of reactions of higher order, the elementary reaction event occurs during the time of collision of such an active molecule with some other molecule. In first-order reactions the elementary event is a result of an energy fluctuation in the molecule itself.

The basic quantitative law of this period in the development of chemical kinetics is a relation between the reaction rate and the temperature, which is expressed in the following formulas:

$$w = Ae^{-E/RT}$$

or

$$\log w = \frac{E}{RT} + B.$$

The value

$$\frac{d \log w}{dT^{-1}} = -\frac{E}{R}$$

should, according to this theory, be constant for any temperature. This classical theory of homogeneous reactions cannot explain a number of cases in which the reaction rate depends much more strongly on tiny traces of impurities than on the concentration of the main substances (positive and negative catalysis). The simple and monotonic dependence of the reaction rate on pressure and temperature given by this theory is also contradicted in a number of cases in which the reaction rate is a very complex and often discontinuous function of pressure and temperature (the boundaries for oxidation of phosphorus, H_2, CO, etc.). Similarly, this theory cannot accommodate a period of induction, when the time enters explicitly in the expression for the rate.

On closer inspection it turns out that the number of reactions that obey the simple laws of the classical theory is incomparably smaller than the number of reactions that contradict this theory.

The extraordinary diversity, complexity, and instability of these phenomena and the lack of any unifying theoretical idea caused many investigators of that period to avoid these phenomena and to exclude them from the sphere of active scientific inquiry. However, in the last few years the situation has changed, and interest in these diverse and complex processes has begun to grow in a geometric progression. The reason for this was the advent of a theory that was capable, although in a general and vague form, of unifying all these phenomena, whose most salient characteristic was that they did not conform to the old theory.

The second period in the development of chemical kinetics is intimately connected with this new theory: the theory of chain reactions. This theory has its roots in photochemistry: the idea of a chain was first introduced by Bodenstein (1913) in an analysis of the photochemical formation of HCl. According to the classical Einstein theory the photochemical yield v of a reaction should equal 1, or, if the secondary reactions are taken into account, should be 2, 3, 4, etc., i.e., in all cases it should be expressed by a

small whole number. At the same time, for the photochemical formation of HCl the number ν turned out to be 100,000. In other words, each absorbed photon caused 100,000 reaction events. Such cases of large quantum yields are observed for many other reactions, provided they are exothermic. Bodenstein hypothesized that the primary reactions caused by the absorption of a photon are only the first link in a chain of reactions. In what follows, ν will denote the length of the chain and will be understood to be the number of all the secondary reactions caused by the appearance of a single reaction center.

The Bodenstein theory has been confirmed in the most varied circumstances and is now considered to be absolutely correct.

We note the following remarkable consequence of this theory: if nothing caused the chain to terminate, it could continue to infinity, i.e., a single initial center would be sufficient to cause the entire mixture to react. Therefore, the reaction is governed not so much by the pressure of the mixture itself as by the presence of slight impurities, which terminate the chains by reacting with their intermediate products. This provides an explanation for negative catalysis. Using oxygen as the impurity, Bodenstein and his colleagues brilliantly confirmed this consequence of the chain theory.

In 1923 Christiansen and Kramers attempted to apply the chain idea to dark reactions, specifically to the decomposition of N_2O_5. In 1924 Christiansen attempted to use chains to explain the negative catalysis effect in thermic reactions. In 1930 Bäckström demonstrated for the example of the oxidation of Na_2SO_3 and benzaldehyde that the reactions forming the chains under the influence of light give the same chains when the reactions occur in the dark. Thus the dark reactions and the photochemical chain reactions differ only in the mechanism of formation of the initial links of the reaction. In the first case they result from the absorption of a photon, and in the second case from collisions between molecules that possess a sufficiently large store of energy.

However, the first papers on dark chain reactions did not make much of an impression, even though they already expressed the main idea of the chain theory in the most general form. In 1928 a great many new phenomena presenting a sharp contradiction to the classical theory were first conclusively established and investigated, independently, in laboratories in Oxford and Leningrad, and the basic theoretical guideposts on the path of development of the new theory were staked out.

Before turning to these new phenomena, let us give the basic mathematical expressions of the chain theory, which, as we have said, was basically formulated by Christiansen and Kramers in 1923. Let n_0 be the number of initial chain links formed per unit time as a result of the thermal motion, and let α be the probability that the chain will not be terminated at a given link (in other words, α is the probability of continuation of the chain). Then very simple calculations lead to the following expression for the reaction rate:

$$w = \frac{n_0}{1-\alpha} = \frac{n_0}{\beta},$$

where β is the probability that the chain will be terminated at a given link. The classical theory, which does not take into account the collision of chains, gives

$$w = n_0 = Ae^{-E/RT}.$$

Thus the result of the chain theory differs from the classical result only by a factor $1/(1-\alpha)$. This factor is clearly equal to the number of elementary reactions in the chain, or, in our terminology, the length of the chain. We note that

$$\nu = \frac{1}{1-\alpha} = \frac{1}{\beta}.$$

Let us now turn to the new data obtained in early 1928 which brought about the rapid development of the whole field of chain reactions.

The role of the walls in chain reactions. When active intermediate products of a chain collide with the walls of the vessel, the further development of the chain is terminated on account of the adsorption of these intermediate products on the walls. In other words, the chain is terminated upon a collision with a wall. Since the length of a chain determines the rate, here we first encounter the factor whereby the size of the volume in which a reaction occurs has an important influence on the rate of the reaction. We now know of many cases in which a deactivating effect of the walls is observed, and this effect is the most characteristic sign of a chain reaction. This effect is intimately connected with another characteristic sign of a chain reaction, viz., the strong catalytic effect of inert gas impurities (argon, nitrogen, etc.).

Although these gases do not take part in the reaction themselves, they interfere with the diffusion of the chains to the walls, thereby lengthening the chains and thus increasing the reaction rate. There is by now a sizable literature on this topic:

1927. Semenov (oxidation of phosphorus).
1928. Hinshelwood (H_2+O_2).
1929. Trifonov (H_2+Cl_2).
1929. Bodenstein and Wagner ($CO+Cl_2$), Jost and Young (H_2+I_2), Semenov (H_2+O_2).
1930. Bäckström (oxidation of benzaldehyde), Hinshelwood (oxidation of PH_3), Schumacher and Sprenger (decomposition of ClO_2).

While the matter of the termination of the chains is relatively clear, the situation as to the initiation of the chains (i.e., the nucleation of the initial centers) is not nearly so well understood. We have suggested (following Christiansen and Kramers) that the initial links of the chains arise as a result of thermal motion. It is quite possible that this hypothesis is correct in some cases while in others it meets with serious difficulties. For example, in the case of the combustion of H_2+O the event that initiates the chain is apparently due to the decomposition of the H_2 molecule into $H+H$ (Marshall), of O_2 into $O+O$, or H_2O into $OH+O$ (Haber and Bonhoeffer). In all these cases it

is easy to show (Semenov, 1929) that the number n_0 is not too small to explain the observed reaction rate. The same is apparently true of the reaction $H_2 + Cl_2$, where the primary event should be the decomposition of Cl_2 into $Cl + Cl$. There is another difficulty concerning the dissociation of the molecules H_2, N_2, and, perhaps, others; according to the as yet unpublished experiments of Shekhter, such a dissociation requires collisions in which the relative energy of the particles is much larger than the dissociation energy. This leads to smaller values of n_0 and so makes less likely the mechanism wherein the initial links of the chain are formed in the volume.

A much more likely hypothesis is that the chains arise at the walls (Semenov, 1929, in connection with the reaction $H_2 + O_2$). This hypothesis can be stated concretely in two ways:

1) In a collision between H_2 or Cl_2 molecules with the walls of the vessel, dissociation can occur by the scheme $H_2 + wall \rightarrow (H \ wall) + H$ (Semenov and Frenkel, 1928). In other words, on account of the energy of adsorption of one of the atoms of a molecule the other atom is ejected into the volume. It is easy to see that the energy required for decomposition of a molecule is expressed in terms of the difference $D - F$, where D denotes the dissociation energy of the molecule in the volume and F is the energy of adsorption of the atoms adsorbed by the wall. Since F is ordinarily equal to several tens of large calories, it will clearly be that much easier for dissociation to occur and, hence, for a chain to be initiated.

2) We know that a reaction almost always occurs more easily on a surface than in the volume. It can be assumed that in the individual surface reaction events the heat of the reaction will not always be given up to the wall but under certain favorable conditions may be imparted to some neighboring molecule, causing dissociation of this molecule and the ejection of dissociation products into the volume (1930).

Unfortunately, at the present time there is no direct and irrefutable proof that the chains originate at the walls. The most direct observations were made in the experiments by Polyakov (1928), who passed a jet of very pure hydrogen above heated palladium and obtained luminescence resembling that of atomic hydrogen in a cold quartz tube at a distance of 20–30 mm from the palladium, and the quartz tube heated up noticeably. This effect continued until the palladium was saturated with hydrogen. Unfortunately, this effect is difficult to reproduce, and the experiments were cut short by the departure of Polyakov from Leningrad; it is therefore impossible to be completely confident of their correctness.

Next, we have the very clever experiment of Bennewitz and Neumann, who studied the torque arising on a system of vanes which were coated on one side with a catalyst. The absence of an effect was interpreted by them as proof that only the primary reaction event occurs on the surface of the catalyst and that the energy released in this event creates a chain of reactions taking place in the volume. If this were true, then the entire theory of catalysis would have to be rebuilt on new foundations. In 1929 the author attempted to find this effect by studying the influence of the diameter of the vessel on the rate of the reaction $H_2 + O_2$ in the presence of a catalyst in the form of a palladium wire extending along the axis of the vessel, but the result of this experiment was negative. Besides these direct, but in my opinion, indecisive experiments, there are a number of indirect conclusions that the chains are initiated at the wall. The most convincing in this regard are the experiments of Haber (1930), who studied the explosion of $H_2 + O_2$ in a space "without walls," by crossing jets of H_2 and O_2, and showed that under these conditions it is very difficult to achieve an explosion. When a quartz filament was introduced at the crossing point of the jets, however, ignition occurred under the same conditions as in the case of an ordinary experiment on explosions in quartz vessels. One should also mention the observations of Garner that suggest that the walls of the vessel have a substantial influence on the ignition conditions. Among the other indirect evidence are the experiments of Christiansen (1929) on the thermic reaction $H_2 + Cl_2$; he believes that the relationships that he obtained can only be explained on the assumption that the Cl atoms needed for initiation of the chain appear as a result of the dissociation of Cl_2 at the walls. Very convincing experiments in this regard were done by Schumacher (1930), who studied the thermic decomposition and explosion of ClO_2; he not only showed that the material and state of the walls substantially determine the reaction rate, but he was also able to explain the dual role of the walls, on the one hand stimulating the reaction (when the chains are initiated on them) and, on the other hand slowing it (when the chains are terminated at them). Unfortunately, there is not enough quantitative data in that paper to enable one to describe the role of the walls by a mathematical formula. In that way one could obtain reliable information on the role of the walls.

It is easy to show that the reaction rate per unit volume of a cylindrical vessel can be written as a function of the radius r of the vessel in four different ways, depending on which of four different assumptions are made concerning the role of the walls:

1. The chains are initiated and terminated in the volume. In this case w is independent of r.

2. The chains are initiated in the volume and terminated on the wall: $w = kr^2$ (Semenov, Trifonov, 1929).

3. The chains are initiated on the wall and terminated in the volume: $w = k/r$.

4. The chains are initiated and terminated on the wall: $w = kr$.

Thus, by varying the diameter of the vessel and studying the reaction rate, one can answer this question with perfect assurance. Unfortunately, this has never been done.

The length of the chain itself might depend on temperature; the number of initial centers n_0 is expressed by the function $Ae^{-E/RT}$, and the quantity $1 - \alpha$ by the function $\psi(T)$. Hence

$$w = \frac{Ae^{-E/RT}}{\psi(T)},$$

while the classical theory gives $w = AE^{-E/RT}$.

Generally speaking, when $\psi(T)$ becomes a function of temperature, the concept of the temperature coefficient of the reaction, which is characteristic for the classical theory, loses meaning. The temperature coefficient, which for chain reactions is expressed through $d \log w/dT^{-1}$, is a variable quantity that depends on temperature (Hinshelwood, H_2+O_2; Schumacher and Sprenger, the decomposition of Cl_2O). In photochemical reactions n_0 is governed by the absorption of light. The length of the chain $1/(1-\alpha)$ is determined directly as the quotient of the number of reacting molecules divided by the number of absorbed photons. As has been shown by Kistiakowsky (1929) and Haber, Harteck, and Farkas (1930), the length of the chains in the photochemical reactions H_2+O_2 and $CO+O_2$ increases rapidly with temperature.

It can be shown that the new form of the temperature dependence of the reaction rate is consistent with the fundamental laws of thermodynamics (Semenov, 1929). In 1929 Semenov gave a preliminary theory for the growth of the length of the chains with temperature. Basically, this theory reduces to the following: the individual elementary reactions in the propagating chain are accompanied by the release of energy. The energy released is initially concentrated in the reaction products. Therefore, higher-energy particles are produced in the gas. For example, let us take the chain of reactions in the case of the photochemical formation of HCl:

$$Cl_2+h\nu=Cl+Cl,$$

1) $Cl+H_2=HCl+H+0$ cal,

2) $H+Cl_2=HCl+Cl+45000$ cal/mole,

3) $Cl+H_2=HCl+H$, etc.
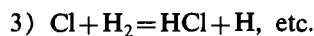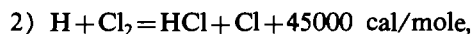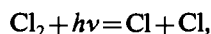
This is how the main chain propagates. However, in each reaction 2) an energy of 45000 cal/mole is released. This energy is initially concentrated entirely in the reaction products HCl and Cl in the form of kinetic or potential energy of these particles. Let us assume that each of the molecules acquires half of the energy, i.e., 23000 cal each.

When these energy-rich particles collide with any Cl_2 molecule, their energy is insufficient for dissociation of the Cl_2 into atoms. This requires 56000 cal. However, if the Cl_2 molecule by virtue of the Maxwellian distribution itself has an energy greater than 33000 cal, the Cl_2 molecule will dissociate on collision into two atoms, which are themselves the initial links of two new chains. Thus a branching of the main chain occurs. The probability of such a branching is determined by the probability that the Cl or HCl atom produced in reaction 2) will have its first collision with a Cl_2 molecule having an energy of 56000–23000 $=33000$ cal. This probability is obviously equal to $e^{-33000/RT}$. If the length of the main chain is ν_1, then the number of branches in it will be $\nu_1 e^{-33000/RT}$. The length of these secondary chains will again be equal to ν_1. Thus the total number of reactions in the main chain and in the chains created by its first branchings will be

$$\nu_1+2\nu_1^2 e^{-23000/RT}.$$

Each of the secondary chains in turn will create $2\nu_1 e^{-33000/RT}$ branches with a total number of reactions $2\nu_1^2 e^{-33000/RT}$. Since the number of secondary chains is equal to $2\nu_1 e^{-33000/RT}$, the total number of reactions in the main chain, secondary chains, and tertiary chains is

$$\nu_1+2\nu_1^2 e^{-33000/RT}+2\nu_1^3 e^{-2\cdot 33000/RT}.$$

By continuing these arguments, we find that the total number of elementary reactions in the chain, including all of its branches, will be given by

$$\begin{aligned}\nu&=\nu_1(1+2\nu_1\gamma+2\nu_1^2\gamma^2+2\nu_1^3\gamma^3+...)\\&=\nu_1+2\nu_1(\nu_1\gamma+\nu_1^2\gamma^2+\nu_1^3\gamma^3+...)\\&=\nu_1+2\frac{\nu_1^2\gamma}{1-\nu_1\gamma}\\&=\nu_1\left(1+\frac{2\nu_1\gamma}{1-\nu_1\gamma}\right)\\&=\nu_1\frac{1+\nu_1\gamma}{1-\nu_1\gamma},\end{aligned}$$

where $\gamma=e^{-33000/RT}$.

As long as $\nu_1\gamma$ is much less than 1, we can use the formula

$$\nu+\nu_1(1+2\gamma\nu_1)=\nu_1(1+2\nu_1 e^{-33000/RT}).$$

Thus we see that the total length of the chain with all its branches increases with temperature only at sufficiently low temperatures, when practically no branching occurs: $\nu=\nu_1$.

The rate of the dark reaction for the case of H_2+Cl_2 is governed by the quantity $n_0\nu$, where n_0 is the number of primary Cl atoms formed per unit time. If we assume that the Cl atoms are produced as a result of the dissociation of Cl_2 into atoms in the volume on collision of the Cl_2 with any other particle having an energy greater than 56000, then

$$n_0=Ae^{-56000/RT}$$

and

$$\begin{aligned}w&=n_0\tau\\&=A\nu e^{-56000/RT}\\&\quad+A\nu_1 e^{-56000/RT}(1+2\nu_1 e^{-33000/RT}).\end{aligned}$$

Letting $56000=Q$ and $23000=U$, we obtain a general expression for the reaction rate as a function of the temperature:

$$w=A\nu_1 e^{-Q/RT}[1+2\nu_1 e^{-(Q-U)/RT}],$$

where ν_1 is independent of temperature. We thus obtain in place of the classical law

$$w=Ae^{-E/RT}$$

the more complex law

$$w=Ae^{-E/RT}+Be^{-E_1/RT}.$$

This law is valid only for values of $Be^{-E_1/RT}$ that are small compared to unity. In a more general form this law is expressed by the formula

$$w = Ae^{-E/RT}\frac{1 + Be^{-E_1/RT}}{1 - Be^{-E_1/RT}}.$$

We have demonstrated this for the example of the ignition of phosphorus, sulfur, PH_3, H_2, and CO, where branching of the chain occurs easily.

However, as we have seen for the example $H_2 + Cl_2$, any chain reaction that is exothermic can have occasional branching. The number of these branchings and, hence, the value of α increase with increasing temperature and pressure, reaching, under certain conditions, a value of 1. Consequently, the chain mechanism of explosion can be extended to all chain reactions, without exception.

As we have seen, the reaction rate is given by the formula

$$w = \frac{n_0}{1 - \alpha},$$

where α is the probability of continuation of the chain; in other words, each reaction event causes on average α new chains, and these in turn cause α_2 subsequent chains, etc. We have seen for the example of the reaction $H_2 + Cl_2$ that the value of α would be equal to 1 if the chains were not terminated at the walls of the vessel or as a result of the reaction of active centers with oxygen molecules. A chain can also terminate if the active molecule radiates away the energy necessary for continuation of the chain, and as a result of various other causes. All these causes in general make α less than 1. However, we have also seen for the example of $H_2 + Cl_2$ that sometimes branching of the chains can occur. In this case a single elementary reaction causes 3 new ones. These cases increase the average value of α and can, under certain circumstances, make α greater than 1.

In a number of reactions such a branching of the chain can occur much more frequently than in $H_2 + Cl_2$. For example, in the oxidation of CO the mechanism of the reaction can be represented as: $CO + O = CO_2^*$, $CO_2^* + O_2 = CO_2 + O + O$, $O + CO = CO_2^*$, and so on. Here each reaction event causes two new active centers (O atoms), and α can reach a value of 2. An analogous propagation of the chain occurs in the oxidation of vapors of phosphorus, sulfur, arsenic, PH_3, etc. The first reaction event is evidently the decomposition of O_2 into atoms $O + O$. Although Haber and Bonhoeffer give a number of arguments in favor of a different mechanism for the onset of the reaction, namely, the decomposition of H_2O into $H + OH$, the experiments of Garner on the ignition of dry and moist mixtures of $CO + O_2$ appear to refute this. Whichever of these hypotheses is taken to be correct, one can say that a very large amount of energy is needed to create the initial centers, and they therefore arise very rarely, i.e., the quantity n_0 in our formula for the reaction rate will be very small. Therefore, as long as α is even slightly less than unity the reaction rate will remain small.

It is only when α is extremely close to unity that the reaction rate becomes appreciable, and in an extremely small interval of α it becomes practically infinite.

Thus for $\alpha < 1$

$$w = 0,$$

and for $\alpha \geqslant 1$

$$w = \infty.$$

This is obviously the ignition condition. Since α is a function of the pressure p, at pressures less than a certain p_1 the reaction will hardly occur at all, while at pressures $p \geqslant p_1$ the reaction rate will become extremely large, i.e., ignition will occur.

This surprising effect was detected by the author in the oxidation of vapors of phosphorus, sulfur, CO, and H_2, and by Hinshelwood and Dixon in the oxidation of PH_3. The numerical value of p_1 and its dependence on the dimensions of the vessel, the concentration of inert gas impurities, and other conditions agree beautifully with the quantitative results of the chain theory (Semenov, 1927, 1928, 1929, 1930; Hinshelwood, 1929).

Since the time of van't Hoff there has existed the hypothesis that an explosion is caused by self-heating of the mixture owing to a slow reaction that goes prior to the explosion; this does not apply to the cases under discussion. The fact is that in all these cases the ignition occurs at very low pressures, from 0.01 to 1 mm Hg, and therefore the insignificant amount of material that undergoes transformation prior to the explosion implies immediately that self-heating of the mixture does not occur. At first glance it would seem that this fact cannot be explained from the standpoint of the chain theory either, since the high probability of termination of the chains at the walls at low pressures and the radiation of energy by the CO_2^* molecule in the form of light should make α very small. It must be remembered, however, that in these cases the chains are highly branched, and α can therefore reach a sufficient value. Another fact that does not fit in with the thermal theory is the experimentally observed dependence of the ignition pressure on the dimensions of the vessel and on impurities. Indirect proof of this comes from the circumstance that the critical pressure for explosion p_1 depends very little on temperature.

The nonthermal nature of the ignition in these cases is also confirmed beautifully by the existence of an upper limit. It has been known for over a century that oxygen at a pressure above a certain critical value ceases to react with phosphorus. However, it is sufficient to pump down the oxygen to the critical pressure for vigorous combustion to occur. The ordinary concepts of chemical kinetics and thermal explosion are, of course, completely incapable of explaining the fact that lowering the partial pressure of one of the components increases the reaction rate. It can, however, be explained by the chain theory, as was shown by Semenov and Jorissen.

Even more convincing evidence is the presence of an upper limit for ignition in $H_2 + O_2$ and $CO + O_2$, which was discovered some time ago by Dixon but was brought to

attention as a result of the studies by Hinshelwood (1930) and our laboratory (1930). This fact also explicitly contradicts the thermal theory. It can be explained in general form by the chain theory if it is assumed that α initially increases with pressure and then begins to decline, reaching a value of 1 at the upper pressure limit. However, it is not known what could cause such a peculiar pressure dependence. Haber did experiments in two crossed jets of oxygen and hydrogen, i.e., in a space "without walls." He found that in the temperature region where Garner, Hinshelwood, and we in our laboratory observed the phenomenon of lower and upper limits no explosion occurred at all. However, when a quartz rod was introduced at the crossing point of the jets, ignition occurred as usual. This experiment is a shining demonstration of the fact that the chains are initiated at the walls, and without walls there are neither chains nor a chain-like explosion; however, one can scarcely conclude from this that the upper-limit effect is due to the wall, as Haber attempted to do. His opinion is essentially that high pressure prevents diffusion of active centers into the volume and thereby hinders the explosion; hence, the upper pressure limit for explosion. However, the development of a chain does not require diffusion of centers to an appreciable distance from the walls; it is easy to see that the number of initiated chains will not depend on the pressure in any case. As to the extinction of chains at the walls, here, as we have seen above, the length of the chains first increases rapidly with pressure and then stops growing, but it never falls off with increasing pressure. Thus Haber's explanation must be considered implausible.

It is possible, however, that the presence of an upper limit is due not to the basic laws of chain behavior but to ancillary effects. We have observed on more than one occasion that when a $CO+O_2$ mixture is admitted into a vessel at a pressure below the upper limit, it burns very briefly after ignition and then dies out, so that only 5–10% of the gas is burned up. When gas is pumped out of the vessel the mixture again ignites. There is another fact that pertains to the lower limit. If the mixture is admitted into an empty vessel by rapidly turning a wide valve, ignition begins at a pressure p equal to the lower limit p_1, i.e., at the same values that are obtained in the cleanest conditions of a flowing jet. However, if the mixture is admitted very slowly through a capillary, then in H_2+O_2 and $CO+O_2$ (this effect is absent in phosphorus) ignition occurs only at pressures significantly above the lower limit, and sometimes (in the case of $CO+O_2$) it does not occur at all.

The first experiment proves that the reaction forms some kind of products that poison the reaction. Most likely these products poison the wall and make it incapable of initiating the basic links of the chain. As the pressure of the mixture is lowered the diffusion of these harmful products from the wall into the volume increases, the wall is "cleansed," and the reaction again develops. The second experiment shows that when the mixture is admitted rapidly into the vessel the rate of propagation of the chains is so large that there is not enough time for the poisoning of the walls to occur. When the gas is admitted slowly the explosion is preceded by a slow reaction (for α close to 1),

which develops predominantly near the walls. An elevated concentration of harmful products is created near the walls, so that the walls are poisoned before the conditions for an explosion are created (i.e., $\alpha \geqslant 1$).

This idea can easily explain the existence of an upper limit: the higher the pressure, the more slowly the chains diffuse into the interior of the vessel and, hence, the higher the concentration of the harmful products near the walls and the faster their poisoning occurs. When the pressure reaches a certain limiting value, the rate of poisoning becomes so high that explosion becomes impossible. The harmful products diffuse only very slowly into the volume, and instead of an explosion one has a slow reaction, which has actually been observed by Hinshelwood and by us and which has been discussed in detail by Topley. It is possible that this secondary process is responsible for the upper limit.

It must be noted that all this discussion is not incorporated into the usual mathematical formulation of the chain theory. Indeed, the formula $w=n_0/(1-\alpha)$ gives a rate equal to infinity for any arbitrarily small value of n_0 provided that $\alpha \geqslant 1$.

If this is the case, then under the condition $\alpha > 1$ explosion will occur independently of the degree of poisoning of the walls, for there will always be some number of initial centers n_0.

It seems to me, however, that this formula, which does not take into account the influence of the number of initial centers, is inadequate.

There are a number of facts which indicate that the ignition pressure depends on the number of initial centers. For example, it is indisputable that the ignition of sulfur vapor does not occur under the condition $\alpha > 1$ unless a sufficient number of initial centers is formed on account of a slight ozone impurity in the oxygen (Semenov and Ryabinin, 1928). This fact clearly indicates the important role of the number of initial centers n_0 on the ignition conditions. The inadequacy of the formula $w=n_0/(1-\alpha)$ is manifested with particular clarity in the fact that both in the case of the oxidation of phosphorus and sulfur and in the reactions H_2+O_2 and $CO+O_2$ the reaction rate during combustion, i.e., under the condition $\alpha > 1$, although rather large, is far from being infinite and has some definite value. This also follows from the fact that the ignition of H_2+O_2 can be achieved at low pressures only at temperatures above 440°. As this temperature is approached from above, the ignition pressure suddenly begins to increase rapidly, and, finally, at temperatures below 440°, ignition becomes altogether impossible at any pressures. This fact can easily be explained by the assumption that the number of initial centers decreases with decreasing temperature. At first, as long as n_0 is large, ignition is governed by the condition $\alpha=1$, and, as long as α is not very temperature dependent, neither will be critical pressure be. However, when n_0 is very small, ignition is hindered and will not occur unless α is significantly greater than 1; this causes the sharp growth in the critical pressure for ignition as the temperature is lowered.

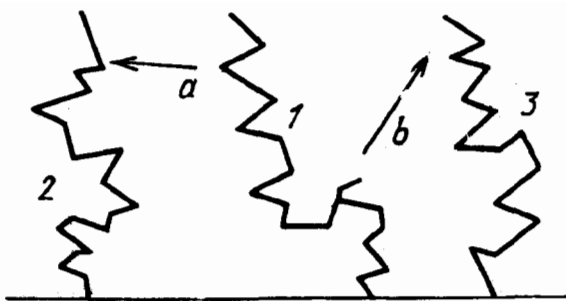Since this growth in pressure begins to affect the afore-

FIG. 1.

FIG. 2.

mentioned poisoning of the walls (the upper limit effect), ignition is altogether impossible below a certain limiting temperature.

Another piece of evidence arguing in favor of this point of view is the fact that a slight NO_2 impurity in the hot mixture strongly lowers the critical temperature for ignition, in the case of $H_2 + O_2$ from 440° to 240 °C. The effect is evidently due to the circumstance that the ease with which an O atom can be split off from NO_2 causes an increase in the number of initial reaction centers and thereby facilitates ignition.

Thus all the facts mentioned suggest that, along with the quantity α, the number of initial centers enters into the conditions governing ignition.

While pondering the question of what is wrong with the formula $w = n_0/(1-\alpha)$, the author originally came to the following conclusion. In all of my previous theoretical arguments I imputed to the quantity α not only the probability of continuation of a chain into the volume but also the probability that a chain will be terminated at the wall, assuming that for any link of the chain there is a single definite probability of collision with the wall that is the same for all links of the chain. This argument can scarcely be correct, since the probability of collision with the wall for an active molecule located far from it is negligibly small, while, conversely, for an active molecule located in the immediate vicinity of the wall this probability is close to 1. In averaging this probability, as I did in my previous papers, I was in effect stating, as is clear from Fig. 1 (here chain 1 is the main chain and 2 and 3 are its branches initiated at links a and b), that the branch chains begin to develop at the same average distance from the wall as the main chain; consequently, chains 2 and 3 have the same length as chain 1. This can hardly be the case. It is much more plausible to assume that the secondary chains begin at the same point at which they are initiated from the main chain, i.e., at points a and b, so that chain 3 is shorter than chain 2, and chain 2 is shorter than chain 1. This is demonstrated in Fig. 2.

It is easy to show that this new assumption leads to the formula

$$w = \frac{n_0(1-\alpha^\nu)}{1-\alpha},$$

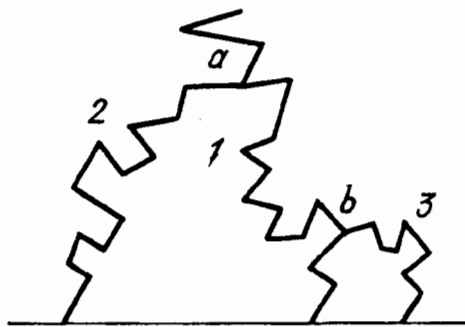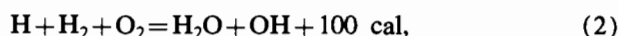where α is the probability of continuation of the chain into the volume and ν is the number of links in the first chain on its path from the point of initiation to the wall. If ν is rather large and $\alpha < 1$, this new formula will agree with the old, since α^ν is small compared to 1. However, for $\alpha = 1$ and also for $\alpha > 1$ the new formula does not give $w = \infty$.

This is how I put the question at the VII Physico-Chemical Conference in the autumn of 1930. Is it or is it not possible to have infinite chains when they are terminated at the walls? In other words, is there some critical condition of the type $\alpha = 1$ at which we obtain a sharp transition from finite chains to infinite chains—a transition from a slow reaction to an explosion? This question was answered by Bursian and Sorokin (1931), who, by applying the diffusion equation to the calculation of chain reactions in an extremely clever way, proved with complete clarity that my doubts were unwarranted, that chains can become infinite upon a transition through a certain critical value, and consequently that all my old arguments remain valid.

However, when α depends on the external conditions and not on the number of initial centers, the experimental evidence presented above, indicating a connection between the ignition conditions and the number of initial centers, remains theoretically inexplicable and at odds with the theory.

I contemplated a way out of this situation in an as yet unpublished paper on the interaction of chains. In order to formulate the theory more clearly, let us discuss it for the particular example of the association of hydrogen with oxygen.

According to Bonhoeffer and Haber (1929) the association reaction $H_2 + O_2$ goes by the following chain scheme:

$$H_2 = 2H \text{(on wall and H escapes into volume)}, \quad (1)$$

$$H + H_2 + O_2 = H_2O + OH + 100 \text{ cal}, \quad (2)$$

$$OH + H_2 = H_2O + H, \text{ etc.} \quad (3)$$

The chains are terminated, for example, at the wall, i.e.,

$$H + \text{wall} = \tfrac{1}{2}H_2, \quad (4)$$

$$OH + \text{wall} = \tfrac{1}{2}H_2 + \tfrac{1}{2}O_2. \quad (5)$$

The branching of the chains remains unclear. I prefer the following mechanism of branching. The large amount of energy released in reaction (2) is concentrated in its products H_2O and OH. Thus one gets an excited molecule H_2O^* which only after a large number of collisions loses its excitation (which exceeds the excitation energy for the total explosion of the gas) according to the reaction

$$H_2O^* + 14 = H_2O + 14. \tag{6}$$

If the H_2O^* molecule, before losing its excess energy, encounters another H_2O^* molecule, then the following reaction is theoretically possible:

$$H_2O^* + H_2O^* = H_2O + H + OH, \tag{7}$$
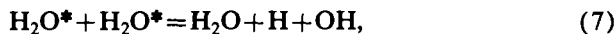
i.e., the reaction associated with the appearance of two new initial links of the chain (branching). The concentration of H_2O^* molecules and, hence, the probability of branching of the chain, will naturally depend on the overall reaction rate, i.e., on the number of initial centers (H atoms), or, in other words, on the rate of reaction (1).

Hence, α will depend on the number of initial centers n_0, and so this number will figure into the ignition condition $\alpha = 1$. The smaller n_0, the more difficult the ignition; QED. I believe that the development of this theory for the interaction of the chains will prove extremely fruitful, especially for the theory of combustion and detonation.

The new formulation, like the old, remains completely incapable of explaining the presence of an induction period between the start of the reaction and the explosion itself. In the explosion of ordinary gaseous mixtures the induction period is often measured in minutes, while the period of total development of each chain cannot be longer than 0.1 s. Even more surprising are the induction periods for explosions occurring under an external influence. For example, in the ignition of sulfur by an ozone impurity, the induction period reaches one minute. In the ignition of a sensitized mixture of $H_2 + O_2$ subjected to light (Haber and Harteck) the explosion occurs several minutes after the luminescence stops.

There are even more surprising examples of induction periods lasting several hours. For example, Schumacher (1930) observed that ClO_2 under certain conditions explodes half an hour after its temperature has reached the explosion point. Roginskiĭ and his co-workers observed that nitroglycerin and trinitrotoluene in closed vessels explode spontaneously several hours after heating, the induction period being precisely determined for each temperature.

All these facts show that there is something in the mechanism of explosions that we still do not understand. Chemists call this by the old term autocatalysis. I think that in general they are right. In such a reaction of explosive materials apparently some kind of products (e.g., the aforementioned NO_2) are formed that under favorable conditions initiate chains more easily than does the main material. Formally speaking, the formation of these products is the beginning of the formation of a chain. But since

these products do not initiate chains immediately after they are formed but rather after a longer or shorter time interval, we arrive at the following conclusions:

1. In the formation of these autocatalytic materials, the secondary chains can start at any point in the volume, and therefore the formula

$$w = \frac{n_0}{1 - \alpha}$$

remains in force.

2. The evolution of the reaction rate is governed not by the propagation of a single chain but by the time that passes between the appearance of the autocatalytic molecule and the time when the chain reaction commences automatically. If γ (> 1) is the average number of autocatalytic molecules arising in the propagation of each molecular chain, then the reaction rate w as a function of time is given by the formula

$$\log w(t) = n_0 \gamma^{t/\tau}.$$

For an explosion to occur it is necessary that the reaction rate reach a certain definite value w_1, which should be rather large. The time T_1 that passes from the start of the process to the time when w becomes equal to w_1 will be the induction period. Clearly it will be longer the larger the value of τ.

All these arguments show that the complex picture of ignition needs a lot more work before it will become completely clear. Nevertheless, we can see that the chain theory is a reliable tool and that, having it, we need not fear the difficulties but can hope that in the not too distant future we will be able to investigate the detailed nature of ignition and explosions. In the study of useful explosions occurring at rather high pressures we cannot ignore the results of the thermal theory of explosions. At high pressures and temperatures the value of n_0 becomes extremely large. Of course, the reaction rate

$$w = \frac{n_0}{1 - \alpha}$$

also reaches significant size, since $\alpha < 1$. The heat evolved in the reaction causes the mixture to heat up and increases n_0 and hence w. If the removal of heat to the outside does not counterbalance the heat released in the reaction, then the mixture will become progressively hotter. This rapid self-heating of the mixture and the very rapid growth of the reaction rate can lead to explosion if $\alpha < 1$. It should be noted that a thermal explosion is theoretically possible for every exothermic reaction, even if it does not involve the formation of chains. But if one analyzes this question carefully, it is easy to see that only in the case when the reaction rate increases very rapidly with temperature can the rate of increase of the reaction rate be sufficiently rapid for an explosion to occur. Thus, for a thermal explosion it is necessary that the temperature coefficient of the reaction or the value of the activation energy E be very large; however, the reaction rate is given by the expression

$$Ae^{-E/RT}$$

in which the larger the value of E, the smaller the value of $e^{-E/RT}$. For an explosion to occur not only must the activation energy be large but so must the absolute value of the reaction rate, i.e., the value of A. A brief calculation shows that the value of A in this case must be abnormally large, much larger than it should be according to the theory of bimolecular and monomolecular reactions. Only the introduction of the chain theory can maintain for A the values required by experiment.

According to this, all the explosive reactions whose kinetics are known turn out to be chain reactions (Hinshelwood, 1928, 1929, 1930). Good proof of the presence of chains in the case of hydrocarbon explosions is the effect of anti-knock agents. According to the theory of Egerton (1928) their effect can easily be explained by a termination of the reaction chains.

In conclusion I would like to say a few words about the mechanism of ignition of cold gaseous mixtures.

It is known that a spark will ignite a gas only if the gas pressure exceeds a certain critical value. Kowalsky has done several experiments on the temperature dependence of the critical pressure for various powers of the spark (the power was determined by the capacitance of the condenser which was discharged to produce the spark). He obtained the series of curves shown by I–III in Fig. 3, in order of increasing power of the spark; curve IV is the ordinary spontaneous-ignition curve taken for the mixture on the same apparatus.

The first remarkable thing is the smooth transition of the lower branch of the spontaneous-ignition curve into the system of artificial-ignition curves. As we have said, at the point T_k the spontaneous ignition stops, since the thermal motion does not produce initial centers in sufficient numbers for the development of explosion.

On the basis of this theory one can conclude that an explosion can be brought on by artificially creating initial
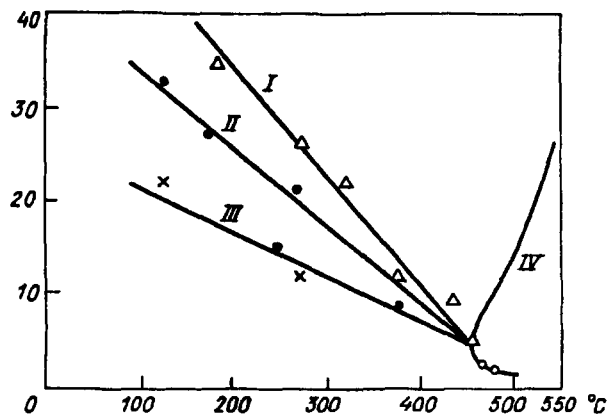

FIG. 3.

centers. The effect of the spark reduces to the creation of these centers. The lower the power of the spark, the higher the critical pressure, as can be seen. This result confirms our new formulation of the theory of chain ignition, according to which the smaller the value of n_0, the higher the pressure necessary for explosion.

Interestingly, in contrast to spontaneous ignition, in spark ignition there is no upper pressure limit. This supports Haber's hypothesis that the upper limit is due to the spontaneous formation of chains at the walls. In artificial ignition the centers arise in the volume, so an upper limit does not exist.

Translated by Steve Torstveit