CHAIN REACTIONS

MAX BODENSTEIN

Physikalisch-Chemisches Institut, Berlin, Germany

The assumption of chain reactions was first used by me in 1913 (1) to interpret the fact that in many photochemical processes the number of reacting molecules is much larger than the number of absorbed quanta. I assumed that by the reaction of the primary light-affected molecule there is formed an unstable intermediate product, rich in energy, which on further reaction gives rise not only to the well-known final product, but also to another intermediate product which regenerates the same process again and again, thus producing a great number of molecules of the final product, starting from one quantum absorbed.

The simplest example is the mechanism proposed later by Nernst for the formation of hydrogen chloride:

$$
\begin{aligned}
Cl_2 + E^1 &= 2\,Cl \\
Cl + H_2 &= HCl + H \\
H + Cl_2 &= HCl + Cl \ldots.
\end{aligned}
$$

That indeed the "Chlorknallgas" gives such a long series of reactions has been shown most clearly by Weigert and Kellermann (2). After an illumination of 10^{-6} seconds they were able to observe a reaction during 2×10^{-2} seconds.

Such a chain may be produced in another way than by active intermediate products. The molecules of the final product must have an excess of energy immediately after their formation. By transferring this energy to the molecules of the starting material,

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[1] E means one Einstein = 6.06×10^{23} quanta, in analogy to F = one Faraday = 6.06×10^{23} electrons. See Bodenstein and Wagner: Z. physik. Chem. **B3**, 456 (1929).

they may activate these also. Using the same example as before, the series would be:

$$Cl_2 + E = Cl_2^{*}\,[2]$$
$$Cl_2^{*} + H_2 = 2\,HCl^{*} \text{ or } HCl^{*} + HCl$$
$$HCl^{*} + Cl_2 = Cl_2^{*} + HCl \ldots.$$

This would be an energy-chain instead of the former matter-chain. But the assumption of such an energy-chain involves a difficulty. That there are specific reactions between Cl and H_2 is evident, but here we must presume that the transfer of energy is specific too, and that the energy passes over from HCl^{*} only to Cl_2, and not to the molecules of the final product or to those of some foreign gas present. Otherwise these molecules would be in competition with those of Cl_2 and ought to check the reaction.

This specificity of energy-transfer seemed at first unlikely, but now there is a good deal of proof that it really exists. For instance, the fluorescence of mercury or sodium vapor excited by the absorption of their own light is extinguished by foreign gases which react quite specifically (3), and a quite similar phenomenon has been observed by Kistiakowski (4) in the photochemical decomposition of ozone. These facts demand that there is a resonance between sender and receiver, and furthermore, that the spheres of action in these processes are much greater than those known from the kinetic theory of gases (5). That would imply that the transferred energy is not a kinetic, but an internal energy, which corresponds exactly to the application of this energy to produce a chemical reaction. This transfer of energy has been treated in the last months from the standpoint of the wave mechanics by Kallman and London (6) and may now be well understood by means of this theory.

The assumption of chain reactions has arisen from photo-

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[2] Cl_2^{*} means an excited molecule. I proposed this interpretation in 1916 (Z. Elektrochem. **22**, 53 (1916)) because my first interpretation, using a free electron as intermediate body, was proved to be impossible, and because the one proposed by Nernst was also thought to be impossible at that time because of an abnormally large heat of dissociation of the chlorine molecule, which rendered the reaction $Cl_2 + E = 2\,Cl$ impossible for quanta of visible light. Today we know that the heat of dissociation of the chlorine is much less, and that this reaction really occurs.

chemistry, but it may be used for reactions in the dark too. Here the first example was in the formation of hydrogen bromide. Nearly twenty-five years ago Lind (7), while working with me in the laboratory of Ostwald, found that there was a very unusual law governing the velocity of this reaction. At that time we did not find an explanation for the observed formula. This explanation was obtained in 1919 by three independent authors,—Herzfeld (8), Polanyi (9) and Christiansen (10). The chain assumed was:

1. $Br_2 = Br + Br$
2. $Br + H_2 = HBr + H$
3. $H + Br_2 = HBr + Br$, but also
4. $H + HBr = H_2 + Br$, and finally
5. $Br + Br = Br_2$

This was without doubt the first discussion of chain reactions occurring without light. It may be mentioned that later we studied the influence of light upon this reaction too, and found that the combination of observations made in the light and in the dark has given important information concerning reaction 5, the first case in which it was possible to investigate the velocity of a reaction between atoms (11).

In the meantime a large number of such chain reactions has been studied in the dark as well as in the light. The theory has also been generalized in two ways and has been applied to some special phenomena, giving very interesting results.

The first generalization was made by Christiansen and Kramers (12) to explain how the heat of activation in many gas reactions could be gained quickly enough by the molecules for them to react. Here the authors have introduced the assumption that the energy is transferred from the products just formed to the reacting molecules by an energy-chain as described above, with the specificity of the energy-transfer which now has become well understood by means of the theory of wave mechanics.

A second generalization was made by Christiansen (13) and verified in some experimental investigations by Bäckström (14). These authors have advanced a theory of negative catalysis, using chain reactions for its explanation.

This theory arose also from photochemistry, especially from the reaction between hydrogen and chlorine. If we use the mechanism mentioned above as suggested by Nernst, or any other mechanism of that kind, it is not obvious why the reaction may come to an end, and why one quantum of absorbed light may not cause the formation of an infinite number of HCl molecules. Now we have known for a long time that oxygen checks the combination of hydrogen and chlorine in a remarkable manner—that it is a negative catalyst for this reaction. Discussing the law of the reaction velocity as governed by the concentrations of H_2, Cl_2 and O_2, one is led to the conclusion that there is a reaction between the hydrogen atom and the oxygen, which uses up the former and thus breaks off the chain (15). It is not quite clear what kind of reaction may occur here, but that this reaction terminates the chain has been shown quite clearly by Miss Cremer (16) in my institute by the fact that for one quantum absorbed one molecule of water is formed, independent of the length of the chain, i.e., independent of the number of HCl molecules formed.

Thus the negative catalyst breaks off the chain in this photochemical reaction. That many cases of negative catalysis may be easily explained in the same way has been predicted by Christiansen and has been proved in excellent investigations by Bäckström.

Let us now speak briefly of some further applications of the idea of chain reactions. Very interesting ones have been given recently by Haber and Bonhoeffer (17), also by Hinshelwood (18), Pease (19), Egerton (20), Semenoff (21) and other chemists. The reactions here in question are those occurring in the combustion of fuel gases,—hydrogen, hydrocarbons, and carbon monoxide. The German chemists have considered the reaction taking place in flames or explosions. With the aid of the spectroscope and our well-improved knowledge of spectra, and using our knowledge concerning the heats of dissociation of H_2, O_2, the C—C linkage and so on, they were able to find out what sort of intermediate molecules were formed between the starting substances and the final products. They observed the formation of OH, CH, CC and other unstable materials. They were also able to answer the question as to how the chains are broken off—namely, by the loss of energy in the form of the radiations which give the special colors to the different flames or explosions.

The same reactions have been studied in many investigations from the standpoint of chemical kinetics. That is of course impossible when using flames or explosions, as it is necessary to work with lower temperatures in order to gain a moderate reaction velocity. In all these investigations it has been shown that the place where reaction occurred was not in the gas phase but on the walls of the vessels. It has been known for a long time that there is a narrow domain of a gas reaction of measurable velocity (22) between the temperatures of these wall-reactions and that of explosion. This small domain of temperature has now been studied by the above-mentioned authors, who have discovered that the combustions are chain reactions also, and that the chains are broken off by the walls. This result may be astonishing at first sight, especially since at slightly lower temperatures the reaction takes place on the walls exclusively; but it has been proved quite certainly, and it is after all not difficult to understand, since it is clear that the wall surface is able to take up the energy of the newly formed molecules as well as to adsorb unstable intermediate products, thus giving them occasion to combine with each other.

The idea that the combustions of gases are chain reactions, and that the chains are broken off on the walls or on other solid bodies present, has led to an explanation of the action of the antiknock materials used with easily combustible fuels in internal combustion motors. These antiknock compounds, vapors of lead tetraethyl or of pentacarbonyl of iron, added in small quantities to the hydrocarbon fuels before they are mixed with air and compressed, are decomposed by the high temperature produced by this compression, thus giving rise to a dust of metal or metallic oxide. This dust, present throughout the whole mass of the gases, breaks the chains of the combustion of the benzenes which would otherwise lead to a premature explosion of the mixture and thus to the knocking of the motor.

This is the theory of the action of antiknock compounds as given by Egerton. It may be said that it seems not quite certain whether the substances really cause a breaking-off of the chains on the surfaces of the dust particles. It may be that the "antiknocks" are negative catalysts in the sense suggested by Bäckström, and stop the combustion chain by being oxidized by the intermediate products of these chains. As far as I am aware no proper decision has yet been given as to their mode of action, but in both cases they act as inhibitors of combustion by breaking off the reaction chains.

There are some more applications and some further developments of the idea of chain reactions, but I think that this may be sufficient to give an account of the subject and to show how commonly chain reactions appear, at least in gaseous reactions.

It seems to me that chain reactions will become much more usual in proportion as gas reactions are studied more and more closely. It is not easy in every case to state that some reaction under investigation needs a chain for being completed. I said above that I was led to the assumption of the chains by the fact that in many photochemical reactions the number of reacting molecules was much greater than that of absorbed quanta. But at that time the Einstein law, which demands the identity of both of these numbers, was quite new, and seemed to be a somewhat bold postulate which one could either accept or reject, as was done at that time by other scientists.

But I found that the yield by the photochemical processes was not only too great, but was also dependent upon the concentration of the reacting substances, upon apparently foreign additions, and in many cases upon the temperature, and that these processes showed in many details the characteristic properties of purely chemical reactions. So I was led to treat them in the usual way for treating reactions in the dark,—to look for a law giving a relation between reaction velocity and concentration, and to try to find out in this way the nature of the intermediate products. This is not possible in all cases, but sometimes it has been very successful. Moreover, this is the way by which to decide in every case whether a reaction is a simple one or whether it involves chains.

To illustrate this method, permit me to consider a special case which was investigated in an unusually successful manner a few months ago in my laboratory by Dr. Schumacher. The reaction was the decomposition of ozone, as catalyzed by chlorine, easily measurable in the dark at a temperature of 50°. The measurements indicated that there is a rather long period of induction, due certainly to the reaction itself and not to impurities, and that after this period of induction the velocity is given by

$$\frac{-\,d(O_3)}{dt} = k(Cl_2)^{\frac{1}{2}}\,(O_3)^{\frac{3}{2}}$$

We assumed the following series of reactions:

1. $Cl_2 + O_3 = ClO + ClO_2$
2. $ClO_2 + O_3 = ClO_3 + O_2$
3. $ClO_3 + O_3 = ClO_2 + 2\,O_2$
4. $ClO_3 + ClO_3 = Cl_2 + 3\,O_2$
5. $ClO + ClO = Cl_2 + O_2$

Calculating the velocity of each of these reactions as given by a constant $k_1k_2\ldots$, and the concentration of the reacting substances, we get a series of equations for the velocity of the change in concentration of each of the substances occurring in this scheme. So for ClO_2, for instance, we get

$$\frac{+\,d(ClO_2)}{dt} = k_1(Cl_2)\,(O_3) + k_3(ClO_3)\cdot(O_3) - k_2(ClO_2)\cdot(O_3)$$

If we assume that as soon as the induction period has been completed, the velocities of formation and of using up this intermediate product are equal to each other, for a period of time short in comparison with that of the main reaction, then we may put the whole $\frac{d(ClO_2)}{dt} = 0$. Doing the same with the analogous equations for the other intermediate products, we obtain equations which give the concentrations of the intermediate products expressed by a function of the concentrations of the well-known measurable substances.

So we find in this case

$$(\mathrm{ClO_3}) = \sqrt{\frac{k_1}{k_4}\cdot(\mathrm{Cl_2})\cdot(\mathrm{O_3})} \qquad \mathrm{ClO_2} = \frac{k_3}{k_2}\sqrt{\frac{k_1}{k_4}\cdot(\mathrm{Cl_2})\cdot(\mathrm{O_3})}$$

and for the velocity of decomposition of ozone,

$$\frac{-\,d(\mathrm{O_3})}{dt} = k_1(\mathrm{Cl_2})\cdot(\mathrm{O_3}) + k_2\cdot(\mathrm{ClO_2})\cdot(\mathrm{O_3}) + k_3\cdot(\mathrm{ClO_3})\cdot(\mathrm{O_3}).$$

Neglecting the first term as very small in comparison with the other ones,

$$\frac{-\,d(\mathrm{O_3})}{dt} = 2\,k_3\sqrt{\frac{k_1}{k_4}\cdot(\mathrm{Cl_2})\cdot(\mathrm{O_3})}\cdot(\mathrm{O_3})$$

This is the result as given by the experimental data. Of course, some simplifying assumptions were made in this calculation. In most cases justification is proved only by the fact that the equation calculated in this way agrees with that found by experiment. In this special case, where the induction period was very long, which implies that the constants of the intermediate reactions were measurably small, we were able to calculate all the single k's, thus verifying the validity of the assumptions made.

It is impossible to go into details with this reaction, which is in many respects especially interesting, but I hope to have shown, using this example, that the chain reactions which occur so frequently may be recognized with all desirable certainty by a careful measurement of the reaction velocity, even in those cases where it is impossible to know the number of the primary reacting molecules, as in photochemical processes.

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