SOME GENERAL CONSIDERATIONS IN CONNECTION WITH THE CHAIN-REACTION THEORY.

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Physical chemistry, as a science, has been mostly concerned with the study of chemical equilibrium, without having been able to throw sufficient light on the kinetics of chemical reactions. The real domain of physical chemistry lay in the investigation of the state of equilibrium of a system with a distribution of energy according to Maxwell's law in which thermodynamics provides the means of a quantitative control. If we consider chemical processes from the standpoint of thermodynamics, (*i.e.*, if we think of them as of a series of slowly developing successive states of equilibrium), we are able only to trace the relation between the initial and the final state of the system without, however, being offered any possibilities as to a theory of chemical dynamics in which the object of investigation would consist in tracing the evolution of the process.

Every physico-chemical process is mainly characterised by the fact that the distribution of energy, while the process is going on, no longer follows Maxwell's law, with the result that the parameters of equilibrium—temperature especially—become more or less deprived of meaning. If the deviation from Maxwell's law is not too great (as in the case of thermal conductivity or diffusion, for instance), the conception of temperature can still be maintained by attributing to every point of the space a definite temperature at any definite moment. Substituting, for the rather complex phenomena of deviations from Maxwell's law, the derivative of this local temperature as a function of time and space easily gives the mathematical characteristics of processes of this kind to which later on the term of " quasi-steady " processes will be applied.

Until recently chemical processes were considered to belong to the above group ; therefore, the velocity of reaction could be determined as a function of temperature and concentration. According to this conception the speed of a given reaction is an indirect function of the time, depending on the corresponding variations of concentration and temperature.

However, the above view does not seem quite consistent. Even when the velocity of reaction is too small to involve any marked increase in the temperature of the system, the deviation from Maxwell's law can be very considerable, as seen from the following: In order that any two molecules of the initial substance be able to interact they must possess considerable energy of activation, E, by far exceeding the average thermal energy. In other words, the velocity of reaction is characterised only by the extreme end, so to say, the " tail " of the Maxwellian curve.

Each elementary reaction act is accompanied by the liberation of free energy which is concentrated in a few molecules of the chemical products and dissipated only after a sufficiently large number of collisions.

The presence of molecules of high energy generated by the reaction markedly alters the distribution of energy at the " tail " of the Maxwellian curve *i.e.*, the very part on which the velocity of reaction depends. The rest of the curve, it is true, remains practically unchanged, but, as already mentioned, this part is of little interest for chemical kinetics. During the whole process a thermometer immersed in the reaction vessel will continue to record the same temperature as before, because it is by no means affected by the behaviour of a few molecules belonging to the " tail " of the Maxwellian curve ; but, on the other hand, the reaction mostly depends on what happens at the end of the curve and not on the records of the thermometer. Thus the thermometer cannot be considered as the proper means to investigate things from a kinetic point of view. The conception of temperature, therefore, never ought to be applied without reservations to characterize chemical processes.

The kinetic chain reaction theory was a first rough attempt made to account for the influence of the above-mentioned deviations from Maxwell's law on the velocity of reaction without having to sacrifice the conception of temperature. The idea was this :

Let us suppose the distribution of energy to follow Maxwell's law.

Then, in the unit time there will take place n_0 elementary reactions due to the collisions of molecules carrying the energy E. The amount of energy Q liberated during each single reaction will remain in the products of reaction during a time-interval τ before it undergoes dissipation. If, at the expense of the excess of their energy, the molecules succeed during the interval τ in activating new molecules of the initial substance, then the primary reaction causes a secondary one and so on, thus involving a chain of reactions.

If by α we denote the probability of the chain continuing, the equation which determines the velocity of reaction will be :

$$\tau \frac{dw}{dt} = n_0 + (\alpha - 1)w,$$

whence
$$w = \frac{n_0}{1 - \alpha}\left(1 - e^{-\frac{1-\alpha}{\tau}t}\right).$$

If the energy of a primary reaction be sufficient to cause two secondary ones, α may happen to become larger than unity. In this case

$$w = \frac{n_0}{\alpha - 1}\left(e^{\frac{\alpha-1}{\tau}t} - 1\right).$$

As well known, the theory of chain reactions enabled us to understand many reactions of which the behaviour was not quite clear from the standpoint of older theories. The number of reactions thus examined is very large, and we may consider every reaction to be more or less of the chain type.

However, the chain reaction theory is only a rough approximation ; the assumption of n_0 being a function of temperature is not quite correct, inasmuch as the considerable deviation from Maxwell's law alters the value of n_0. In general, the classification of reactions into primary and secondary ones does not seem consistent. Indeed, we have to deal with an altered distribution of energy, and if only we succeeded in calculating this altered distribution, it would mean the possibility of calculating the velocity of reaction too, but, as this altered distribution, in its turn, is a function of velocity the method leads to very complicated integral equations.

According to the above theory, the rate of dissipation, which as a first approximation is expressed by τ, is a constant whose value varies from one reaction to another ; this constant has about the same fundamental meaning as heat capacity in the theory of equilibrium.

As the existence of swift moving molecules is due to collisions of slower ones, the influence of temperature on the kinetics of chemical reactions perhaps is not so negligible as we have stated above. However, it is easy to prove that, making some appropriate assumptions, slowly proceeding reactions can be imagined in which the velocity does not depend on temperature.

Let us assume an extremely low temperature, so low in fact that practically not a single molecule will carry the energy E sufficient for activation ; let us further suppose a reaction showing marked *ramifications* and denote by δ the probability of a branch appearing in the given link. Now let us suppose that the chain breaks up when two active molecules meet (as is often the case when the active centres are formed by atoms whose recombination leads to a breach of the chain). The probability of the chain breaking up will be $\beta = \beta_0 n$, where n is the number of active centres in unit volume. Then $\alpha = 1 + \delta - \beta_0 n$.

On the other hand, the velocity of reaction w is directly proportional to n; in other words, $\alpha = 1 + \delta - \gamma w$, where $\gamma w = \beta_0 n$.

So long as there are no initial centres formed the reaction does not start. The moment a certain amount of centres is generated artificially (by exposure to illumination or electric discharge) the velocity of reaction increases automatically after the corresponding agent has been removed. Then

$$\tau \frac{dw}{dt} = -(1 - \alpha)w = (\alpha - 1)w = (\delta - \gamma w)w,$$

whence

$$\frac{\delta - \gamma w}{w} = + ke^{-\frac{\delta t}{\tau}},$$

where the value and sign of k depends on the number of initial centres artificially generated at the beginning of the process. Then

$$w = \frac{\delta}{\gamma + ke^{-\frac{\delta t}{\tau}}}.$$

The velocity of reaction increases with time approaching the constant value $w = \frac{\delta}{\gamma}$ independently of the number of centres formed initially. Thus we obtain a definite constant velocity of reaction wholly independent of temperature (the values of γ and δ being so).

Some evidence as to the existence of reactions of the above kind is to be found in recent papers.

Haber, Farkas and Harteck,[1] for instance, have shown that after a short exposure to illumination the reaction $H_2 + O_2 +$ (and similarly $CO + O_2$) continues in the dark during several minutes; in these experiments the mixture of the corresponding gases ($H_2 + O_2$, or $CO + O_2$) has been taken at 400° C. and sensitised by a slight amount of NH_3, conditions at which normally the technical process does not proceed at all.

Schumacher and Stieger [2] noticed a still more surprising fact when studying the dissociation of ClO_2 in the presence of CO; the explosion of ClO_2 causes the oxidation of CO, the process going on at a slow rate during several days without special exposure to illumination and at a temperature of 45° C. until the whole amount of the gases has combined into CO_2.

Let us now consider the influence of the second parameter characterising the state of equilibrium, *i.e.* concentration.

The probability of the molecules of the initial substances being activated by the molecules of high energy generated by the reaction during the time these molecules are still keeping their energy decreases as the concentration of the initial substances becomes less and the products of reaction are accumulating. According to the chain reaction theory the probability α is diminishing as the reaction is going on. It follows that, at the state of equilibrium, the velocity of the reaction, both the direct and the compensating reverse one, can decrease many times (and often some thousand times) as compared with that of the initial phase which is far from equilibrium.

The problem of pseudo-equilibrium is thus again put forth on new theoretical foundations. There is no doubt that in practice we often have to deal with the above state of pseudo-equilibrium. For instance,

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[1] *Z. Elektrochem.*, **36**, 711, 1930.

[2] *Z. Physik. Chem.*, **7B**, 363, 1930.

at definite conditions of pressure and temperature, the reactions $H_2 + O_2$, $P_4 + O_2$, etc., proceed with large velocity, being at the same time isothermal reactions. However, they never reach the state of equilibrium, and stop much sooner, when there still remains a somewhat large amount of the initial substances not having yet interacted. Thus, apparently, we ought seriously to reconsider the conception of equilibrium as a state where two reactions are proceeding with large velocity in opposite directions and balancing each other. In most cases the process is unidirectional until a definite moment and practically stops before a fairly good equilibrium has been reached. (Of course, after a sufficiently long time-interval true equilibrium will be established even here.)

There seems to be no reason to extend to all chemical processes the conclusions arrived at for reactions of a decidedly chain character. Nevertheless, the question arises whether the liberation of free energy in a chemical system ought not to be considered as the most important if not the sole agency determining the rate of the reaction ; and, further, whether the rôle of any catalyst does not mainly consist in preventing the dissipation of the energy thus generated (by formation of intermediate products, for instance).

The above point of view emphasises the foremost importance of the self-evolution of chemical processes, while other factors (such as temperature, concentration, catalysts and so on) are believed only more or less to help in creating suitable conditions for the action of the chemical forces. In previous theories, on the contrary, these factors were considered to play the principal part.

The new conception of the rôle of free energy in chemical kinetics is somewhat analogous to the question of energy in thermodynamics ; it seems very interesting to look also in chemistry for a general kinetic principle similar to that of equilibrium known as the second law of thermodynamics.

My attempts towards this end have not proved satisfactory as yet. I hope there exist no serious objections against the problem being treated in such a general way and would be glad if other workers interested in the theory of the problem attacked it successfully.