

ON THE EXTENSION OF THE CONCEPT OF THE FOUR STAGE MECHANISM. I. GENERAL CONSIDERATIONS

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The authors dealt with the application of the method of the four stage mechanism in such cases, in which the condition laid down in the existence of the rate controlling process in each of the starting, chain, branching and rupturing reaction categories is not fulfilled. They suggest an idea, which seems to be applicable in the case of non-branching chain reactions, namely the postulate of the equality of the two reaction rates, with which the active radicals propagating the chain transform themselves in each other.

They illustrate how the idea can be explained regarding the thermal decomposition of the sulphuric oxychloride to establish the system of rate equations based on the mechanism supported by previous investigations published in the literature.

In the kinetic characterization of complex chemical processes Z. G. SZABÓ [1]—[3] introduced a method with the four stage mechanism, which renders possible to bring into correlation the concentrations of the particles fundamentally important from the viewpoint of the proceeding of the reaction, *i. e.*, those of the reacting substance and the active radicals. The method characterizes the course of the process by means of two differential equations, which correlate the two differential quotients $\frac{dn}{dt}$ and $\frac{dc}{dt}$ of the concentrations of the active radicals and the reacting substance with the concentrations in question n and c in the following way:

$$\frac{dn}{dt} = k_1 c^\lambda + k_3 c n - k_4 n^\mu, \quad (1)$$

$$-\frac{dc}{dt} = k_1 c^\lambda + k_2 c n, \quad (2)$$

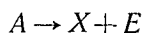
where the terms $k_1 c^\lambda$, $k_2 c n$, $k_3 c n$, $k_4 n^\mu$ on the right sides of the equations denote the rates of the starting, chain, branching and rupturing reactions respectively, λ , $\mu = 1, 2$ depending on whether the starting and rupturing reactions are of first or second order.

The condition of the characterizability of a process by equations of type (1) and (2) is the existence of a rate controlling process in each of the categories starting, chain, branching and rupturing reactions, which denotes the existence of a significantly slowest reaction among successive elementary

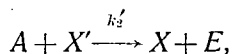
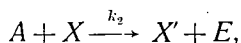
processes, and that of a remarkable fastest among the simultaneous ones. In case of fulfilment of this condition the explanation of the kinetics is considerably simplified by the possibility of the selection of one of the different types of active radicals as their representant, whose concentration's change can be regarded as expressing the change of the concentration of the active radicals in general.

If the condition introduced with the selectibility of the rate controlling processes is not fulfilled, there are some modifications to be made in treating the system of the rate equations of the mechanism, and in different ways, depending on whether the non-selectibility of the rate controlling process takes place in a category of successive reactions or in that of simultaneous ones. The modification denotes the extension of the scheme and to carry it out on the basis of the experiences available at present there are no general methods, it can occur in any case under taking into account the mechanism of the process. *E.g.*, investigating the decomposition of ozon catalysed by chlorine [4], where two elementary reactions of commensurable rate took place among simultaneous rupturing reactions, the extension was possible by representing the rupturing reaction category by two rate components in such a way that the type of the system of the rate equations remained unchanged, *i.e.*, suitable to treat it in the same manner as the original system of differential equations of the four stage mechanism.

Recently the kinetic investigations in the Institute for Inorganic and Analytical Chemistry of the University, Szeged, in the study of the thermal decomposition of the sulphuric oxychloride [4] led to results, the interpretation of which showed the presence of reactions of commensurable rate in both successive and simultaneous reaction categories. The discussion of the kinetics in the case of such a reaction seems to require in the first consideration the completion of the system of the rate equation with a further differential equation. With the aim of illustrating the relations it should be taken into account the scheme expressing the proceeding of the chain by the alternation of the reactions of two different radicals, *i.e.*, in which the starting reaction



is followed by both alternating elementary reactions of the chain



the rates of which are commensurable (X and X' denote the active radicals, E end product molecules, A the initial substance). In this case the faster reaction of the chain do not involve the immediate regeneration of the radicals propagating the slower chain step, consequently the total concentration of the active radicals can not be substituted by the concentration of the active radicals playing role in the slower step of the chain. Thus for basis that feature of the distribution is to be taken that the concentrations of the different types of the active radicals are commensurable, which requires to take into account both the concentration changes of the two active radicals and to

treat the course of the reaction by means of a system of three differential equations

$$-\frac{dc}{dt} = P_1(c, n_1, n_2), \quad (3)$$

$$\frac{dn_1}{dt} = P_2(c, n_1, n_2), \quad (4)$$

$$\frac{dn_2}{dt} = P_3(c, n_1, n_2), \quad (5)$$

where n_1 and n_2 denotes the concentrations of the active radicals X and X' respectively, P_1, P_2, P_3 are polinomials composed of simple expressions at most of third order of their variables.

Fulfilling certain conditions, however, the possibility of a treatment according to an analogous system of rate equations as that of the four stage mechanism (1)—(2) may be given, even in the case of this commensurability of the alternating chain reactions. Thus for example in the case of non-branching chains a simple connexion can be established between the concentrations of the two types of active radicals, when the chain length is sufficiently large. The ground of this connexion is the assumption that one of the active radicals exerts in the chain the same conversion as the other, the formulation of which $k_2cn_1 = k'_2cn_2$ gives simply $n_1 : n_2 = k'_2 : k_2$. Hence, denoting by n the total concentration of the active radicals, one gets according to a simple calculation

$$n_1 = \frac{k'_2}{k_2 + k'_2} n \quad \text{and} \quad n_2 = \frac{k_2}{k_2 + k'_2} n. \quad (6)$$

The substitution of these expressions allows the reduction of equations (4) and (5) to a single equation

$$\frac{dn}{dt} = \frac{d(n_1 + n_2)}{dt} = P_2(c, n) + P_3(c, n), \quad (7)$$

where $P_2(c, n)$ and $P_3(c, n)$ denote the polinomials arising from the P_2 and P_3 of equations (4) and (5) by the substitutions (6).

The above consideration can not be regarded of course as the solution of the question in general, since the very variable feature of the chemical processes may lead in many other ways to the necessity of a similar extension. In spite of this variability the content of the idea expressed in the equation $k_2cn_1 = k'_2cn_2$ — by its suitable reevaluation — may be applied under more general conditions of non-branching chain reactions for carrying out the extension of the scheme. The essential content of the above equality is namely not only the agreement of the contributions of the two types of active radicals in the conversion, but the fact too that within the chain there is no generation of radicals. (In fact, k_2cn_1 is the rate of the transformation $X \rightarrow X'$, k'_2cn_2 that of the regeneration $X' \rightarrow X$.) In this formulation the application of the idea can be tried in general in the treating of non-branching chain reactions in order to reduce the system of the rate equations corresponding to (3)—(5) in the manner treated above. From this trial such a