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Abstract

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A Method for Determining the Rates and Kinetic Constants of Complex Chemical Reactions Occurring in a Flow

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As we have shown (1), from the experimentally found dependence of the conversion of the initial substance on the rate of feed of the substance, it is easy to find the rate of a chemical reaction without knowing the kinetic equation of the process. The dependence of the reaction rate on temperature at a specified constant conversion of the initial substance makes it possible to determine the value of the activation energy of the process. From the value of the activation energy of a heterogeneous-catalytic process and its dependence on temperature, one can judge the region in which the process proceeds.

The proposed method, considered for examples of simple reactions (1), is valid, as is easy to see, only in those cases in which the reaction rate is a function of the conversion of the initial substance, the amount of which in relative units is equal to x, i.e., $W = f(x)$, and does not depend on the number of moles of this substance n_0 fed to the reactor per unit time.

Since the reaction rate is a function of the partial pressures of the reacting substances P_{A_i}, the dependence of W on n_0 will be determined by the dependence of P_{A_i} on n_0. The latter, as was shown (2), can be expressed through the degree of conversion of one of the reacting substances by the relation

$$P_{A_i} = \frac{\dfrac{n_{0A_i}}{n_{0A_1}} - \dfrac{\nu_i}{\nu_1} x_{A_1}}{\dfrac{\sum n_{0A_i}}{n_{0A_1}} - \dfrac{\sum \nu_i}{\nu_1} x_{A_i}} P_o, \tag{1}$$

where ν_i are the stoichiometric coefficients; P_o is the total pressure in the reactor.

It is seen from expression (1) that the quantity P_{A_i} does not depend on n_0 in two cases: 1) when one substance reacts and 2) when several substances react, but in all experiments the composition of the reaction mixture remains constant, and only the feed rate into the reactor of the reaction mixture of the given composition is changed.

In the more general case, when several substances react and the composition of the reaction mixture is different in all cases, the reaction rate will be a function not only of the amount of converted substance x, but also of the feed rate of the initial substance n_0. Therefore, applying to the previously obtained expression for heterogeneous-catalytic reactions (^{1})

$$-\frac{S_0 l}{n_0^2} = \frac{d}{dn_0} \int_0^x \frac{dx}{W} \tag{2}$$

the theorem on differentiation of a definite integral with respect to a parameter, we obtain

$$-\frac{S_0 l}{n_0^2} = \int_0^x \frac{\partial}{\partial n_0} \left(\frac{1}{W} \right) dx + \frac{1}{W} \frac{dx}{dn_0}, \tag{3}$$

where S_0 is the surface area of the catalyst per unit length of its bed in the reactor, and l is the length of the reaction zone.

If the quantity W does not depend on n_0, then expression (3) becomes the previously derived relation (1)

$$W = -\frac{n_0^2}{S_0 l} \frac{dx}{dn_0} = \frac{1}{S_0 l} \frac{dx}{d(1/n_0)}. \tag{4}$$

We used this expression to determine kinetic quantities in the case of simple reactions. The developed method can also be successfully applied to the kinetic description of complex reactions.

A number of industrially important reactions (cracking of individual hydrocarbons and petroleum fractions, dehydrogenation of hydrocarbons, dehydration of alcohols, etc.) proceed through the formation of a stable intermediate product. For example, catalytic cracking proceeds according to the scheme:

$$\begin{aligned} \mathrm{A} \xrightarrow{W_1} \nu_1 &\mathrm{B} + \nu_2 \mathrm{D} + \nu_3 \mathrm{C} \\ &\xrightarrow[W_2]{} \nu_4 \mathrm{D} + \nu_5 \mathrm{C}, \end{aligned}$$

where A is the starting substance, B is the intermediate product, and C and D are the final products. The reaction rates W_1 and W_2 are measured from the conversions of substances A and B.

Analysis of the kinetics of the first stage of a consecutive reaction presents no difficulties. To obtain relations for the kinetic analysis of the second stage of the reaction, let us denote the relative degree of conversion of substance B by y, its relative yield by u, and the relative yield of reaction product C by z (all as fractions of the amount of substance A passed per unit time). Then the rate of the second stage of the reaction can be written as

$$W_2 = \frac{n_0 dy}{S_0 dl}. \tag{5}$$

Taking into account that

$$W_2 = k_2 \sigma_{\mathrm{B}}, \tag{6}$$

where σ_{B} is the degree of filling of the surface by substance B, and that σ_{B} does not depend on the magnitude of n_0, i.e.,

$$\sigma_{\mathrm{B}} = \varphi_1(x, y) = \varphi_2(x, u), \tag{7}$$

using the procedure described above (we integrate (5) and differentiate the resulting expression with respect to n_0), we find:

$$W_2 = -\frac{n_0^2}{S_0 l} \frac{dy}{dn_0}. \tag{8}$$

However, the experiment gives us not the quantity y, but the quantity u of the relative yield of intermediate product B. For the case under consideration, $u = \nu_1 x - y$. To pass from the variable y to the variable u, we seek the difference $\nu_1 W_1 - W_2$. On the basis of formulas (4) and (8),

$$\nu_1 W_1 - W_2 = -\frac{n_0^2}{S_0 l} \frac{\nu_1 dx - dy}{dn_0} = -\frac{n_0^2}{S_0 l} \frac{du}{dn_0}, \tag{9}$$

whence

$$W_2 = -\frac{n_0^2}{S_0 l} \left(\frac{\nu_1 dx}{dn_0} - \frac{du}{dn_0} \right) = \frac{1}{S_0 l} \left[\frac{\nu_1 dx}{d(1/n_0)} - \frac{du}{d(1/n_0)} \right]. \tag{10}$$

The quantity du/dn_0 can be found from the experimental dependence of the yield of intermediate product B on the feed rate of starting material A. In the particular case when the yield of the intermediate product passes through a maximum, $du/dn_0 = 0$, and the following relation holds:

$$W_2 = \nu_1 W_1. \tag{11}$$

Knowing the reaction rate at different temperatures and product concentrations, it is not difficult to find other kinetic quantities as well. For example, the

Fig. 1. Selection of points for determining the activation energy of the second stage of a consecutive reaction (left) and a complex parallel reaction (right)

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activation energy of the second stage can be found from the change in the reaction rate with temperature at a constant value of σ_B. But since σ_B is determined by the variables x and y, or, equivalently, x and u, one must choose for the calculation such a degree of conversion x at which identical values of u are obtained for all temperatures (see Fig. 1). If such a degree of conversion has been found, then, after determining the reaction rates for the points found, it is not difficult to calculate the activation energy. The error of such a determination will be somewhat higher than in the analysis of the first stage of the reaction, because of the superposition of errors in determining the quantities x and u.

Fig. 1. Selection of points for determining the activation energy of the second stage of a consecutive reaction (left) and a complex parallel reaction (right)

If, however, one of the reaction products is formed only in the second stage (for example product C, $\nu_3 = 0$), then the rate of the second stage can be expressed through the relative yield of this product. Since in this case $y = \dfrac{\nu_1}{\nu_5} z$, then, applying this relation to (8), we find

$$W_2 = -\frac{(\nu_1/\nu_5) n_0^2}{S_0 l} \frac{dz}{dn_0} = \frac{\nu_1/\nu_5}{S_0 l} \frac{dz}{d(1/n_0)}. \tag{12}$$

As another example, let us consider a parallel reaction of the type:

$$\nu' A_1 + \nu'' A_2 + \cdots \begin{array}{c} \overset{W_1}{\nearrow} \\ \xrightarrow{W_2} \\ \cdots \\ \underset{W_n}{\searrow} \end{array} \begin{array}{l} \nu_1' B_1' + \nu_2' B_2' + \cdots \\ \nu_1'' B_1'' + \nu_2'' B_2'' + \cdots \\ \quad\cdots\cdots\cdots \\ \nu_1^n B_1^n + \nu_2^n B_2^n + \cdots \end{array}$$

The rate of each stage of such a reaction with respect to some substance (for example A_1) can be expressed through the relative yield of the product of the stage under consideration (for example B_1^i). Denoting the relative yield of this product by z_i, we may write:

$$W_i = \frac{(\nu'/\nu_1^i) n_{0A_1} \, dz_i}{S_0 dl}. \tag{13}$$

If the composition of the reaction mixture does not change for the entire series of experiments with different feed rates, then, using the method described above, we obtain

$$W_i = -\frac{(v'/v_1^i)n_{0A_1}^2}{S_0 l}\frac{dz_i}{dn_{0A_1}} = \frac{v'/v_1^i}{S_0 l}\frac{dz_i}{d(1/n_{0A_1})}. \tag{14}$$

Consequently, by studying the change in the relative yield of the products of such a reaction when the feed rate of the initial mixture is varied, one can determine the kinetic characteristics of any stage of the reaction. Assuming that $W_i = k\Pi\sigma_{A_i}$, the activation energy of any stage of a complex parallel reaction can be determined only at those degrees of conversion of substance A_1 to which unchanged yields of each of the reaction products correspond (Fig. 1).

Methods for determining the reaction rate from the yields of the final product can be used not only for complex reactions but also for simple reactions. In the latter case they may also be used to check the correctness of the experiment, for example by comparing the activation energy calculated from curves for the overall degrees of conversion and from curves for the relative yields of the product, or by checking, for a given temperature, the constancy of the ratio of the reaction rates calculated at identical reagent feed rates from the indicated curves.

All the derived relations remain valid also for homogeneous reactions. In this case, in all the expressions obtained, the quantity S_0 is replaced by the quantity ρ—the reactor cross section.

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1. G. M. Panchenkov, Yu. M. Zhorov, *DAN*, **130**, No. 6 (1960).

2. G. M. Panchenkov, Yu. M. Zhorov, Collection of the Journal *Physical Chemistry*, *Kinetics and Catalysis*, Publishing House of the Academy of Sciences of the USSR, 1960, p. 3.

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