A Method for Determining Kinetic Constants and the Regions of Chemical Reactions Carried Out in Flow

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Abstract

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A Method for Determining Kinetic Constants and the Regions of Chemical Reactions Carried Out in Flow

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The widespread use, in laboratory and industrial practice, of chemical processes occurring in flow at constant total pressure has required the development of classical chemical kinetics, which was created for processes occurring at constant volume.

The general equations of the kinetics of flow reactions are given in work ([1]) in the form:
for homogeneous reactions

$$\frac{n_{0A_i}}{\rho}\frac{dx_{A_i}}{dl} = W; \tag{1}$$

for heterogeneous-catalytic reactions

$$\frac{n_{0A_i}}{s_0}\frac{dx_{A_i}}{dl} = W_s, \tag{2}$$

where n_{0A_i} is the feed rate of substance A_i; x_{A_i} is the degree of conversion of substance A_i; ρ and l are, respectively, the cross section and the length of the reaction space; W and W_s are the rates, respectively, of the homogeneous and heterogeneous-catalytic reaction, measured with respect to substance A_i; s_0 is the catalyst surface per unit length of the reaction space.

The most widespread method for studying the kinetics of flow reactions is to investigate the dependence between the degree of conversion x and the feed rate of the reagent n_0. However, the dependence of x on n_0 cannot be directly processed by formulas (1) and (2), since they contain the variables x and l. Therefore, in order to obtain integral kinetic dependences, one must assume a form of the kinetic equation $W = \Phi(x)$, after which integration of equations (1) and (2) becomes possible. If the experimental data correspond to the relations obtained in this way, it is considered that the proposed kinetics is correct.

This method has proved very fruitful and has made it possible to study the kinetics of a number of reactions ([2]). However, in many cases it is difficult

to make an assumption about the form of the kinetic equation. In addition, for heterogeneous-catalytic reactions, when diffusion retardation is present, a distortion of the kinetics is observed; thus, the experiment must be carried out in the kinetic region.

In order to make it possible to determine kinetic constants without assuming a reaction mechanism, and also to determine the region in which the reactions occur, we have developed a graphical method for studying kinetics using experimental curves of the dependence of x on n_0. Using these curves, one can directly measure the reaction rate expressed through the variables x and n_0. For this purpose, let us perform a change of variables in equations (1) and (2) as follows.

Integrating equation (2) with respect to t from 0 to l and with respect to x from 0 to x, we obtain

$$\frac{s_0 l}{n_0} = \int_0^x \frac{dx}{W_s}. \tag{3}$$

Differentiating expression (3) with respect to n_0, we find:

$$-\frac{s_0 l}{n_0^2} = \frac{d\left[\int_0^x \frac{dx}{W_s}\right]}{dx} \frac{dx}{dn_0}, \tag{4}$$

whence

$$W_s = -\frac{n_0^2}{s_0 l} \frac{dx}{dn_0}. \tag{5}$$

Similarly, for homogeneous reactions we find

$$W = -\frac{n_0^2}{\rho l} \frac{dx}{dn_0}. \tag{6}$$

Expressions (5) and (6) make it possible to determine the reaction rate from curves of the dependence of x on n_0, since dx/dn_0 is the tangent of the angle of inclination of the curve to the axis of flow rates. Thus, it becomes possible to study the kinetics of reactions on the basis of experimental data, without specifying the reaction mechanism in advance.

Fig. 1. Experimental curves of the dependence of x on n_0 for cumene cracking at atmospheric pressure on an aluminosilicate catalyst at various temperatures. $dx/dn_0 = -\operatorname{tg}(180^\circ - \varphi_1)\alpha_1$, where α_1 is a coefficient depending on the choice of scale.

Let us consider, for example, a method for determining the activation energy. In the general case, for an irreversible reaction we may write

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$$W_s = k(T)f(C) = Pe^{-E/RT}\psi(C_0, x), \tag{7}$$

where $k(T)$ is the reaction rate constant; P is the pre-exponential factor; E is the activation energy; R is the gas constant; T is the temperature of the experiment; C is the current concentration of the reactant; C_0 is the initial concentration of the reactant.

Equating the right-hand sides of (5) and (7) and taking the logarithm of the resulting equality, we find

$$\ln\left(-n_0^2\frac{dx}{dn_0}\right) = -\frac{E}{R}\frac{1}{T} + \ln P\psi(C_0, x)s_0 l * \tag{8}$$

* As is evident from comparison of (7) with (6), for homogeneous reactions the equation remains the same, but ρ enters it instead of s_0.

or

$$\ln\left(-n_0^2\frac{dx}{dn_0}\right)_{x=x_1} = -\frac{E}{R}\frac{1}{T} + \text{const}_{x=x_1}. \tag{9}$$

Consequently, the dependence of $\ln\left(-n_0^2\frac{dx}{dn_0}\right)$ on $\frac{1}{T}$ is linear at unchanged initial concentrations and degrees of conversion, and the value of the activation energy can be found from the slope of the straight line. At constant total pressure C_0 depends on T, but the change in C_0 with temperature may be neglected in comparison with the change in k. In the case of hydrocarbon cracking $W = \Phi(x)$ ([3]), and relation (5) is exact.

Upon transition into the diffusion region, a decrease in the activation energy is observed, and this leads to curvature of the line $\ln\left(-n_0^2\frac{dx}{dn_0}\right) = F\left(\frac{1}{T}\right)$.

Fig. 2. Dependence of $\ln \text{const}\left(-n_0^2\frac{dx}{dn_0}\right)$ on $\frac{1}{T}$, obtained by treating the curves of Fig. 1 according to formula (9).

1—$x = 0.8$; 2—$x = 0.5$. $\operatorname{tg}\varphi_2 = -\frac{E}{R}a_2$, where a_2 is a coefficient depending on the choice of scale.

Fig. 2. Dependence of ln const $(-n_0^2 dx/dn_0)$ on $1/T$, obtained by treating the curves of Fig. 1 according to formula (9).

Figure 2: Fig. 2. Dependence of ln const $(-n_0^2 dx/dn_0)$ on $1/T$, obtained by treating the curves of Fig. 1 according to formula (9).

Thus we obtain the possibility of measuring the activation energy in the diffusion region, using flow reactors. We note that upon transition into the diffusion region there will also be superimposed the phenomenon of a change in the form of $\psi(C_0, x)$; however, it will have little effect in estimating the activation energy.

We have studied the kinetics of cumene cracking over a wide range of temperatures and space velocities on an industrial aluminosilicate catalyst with a bead size of 0.42 cm. This reaction is used as a model reaction in studying the properties of aluminosilicate catalysts; therefore, it is essential to determine the conditions under which the true kinetics of the reaction are not distorted.

The experiments were carried out with cumene purified from hydroperoxides, which are cracking inhibitors, in a standard flow reactor of the MINKh and GP (for a description of such a reactor see ([4])). From the experimental results, curves of the dependence of x on n_0 were constructed for a number of temperatures; these are shown in Fig. 1, and the experimental and analytical procedure was the same as in earlier work ([5]).

The method set forth above was used to determine the activation energy of cumene cracking in the diffusion and kinetic regions. For this purpose, from Fig. 1 the feed rates and the slopes of the curves were found at the points for which $x = 0.8$ and $x = 0.5$. These quantities were treated according to equation (9); the results are given in Table 1.

From the data of Table 1, curves of the dependence of $\ln \text{const}\left(-n_0^2 \frac{dx}{dn_0}\right)$ on $\frac{1}{T}$ were constructed (Fig. 2). It is seen from Fig. 2 that at low temperatures (the kinetic region) a linear dependence is observed, whereas at high temperatures (the diffusion region) the points form a curve. From Fig. 2 one can find all the regions of the cumene cracking reaction on the catalyst studied, from the change with temperature in the value of the observed activation energy.

Table 1

Processing of experimental curves of the dependence of x on n_0 by means of formula (9)

t, °C	x, mole fractions	$180° - \varphi_1$	$n_0 \cdot 10^5$, mol/sec	$n_0^2 \cdot 10^{10} \times \text{tg}(180° - \varphi_1)$	$\ln [n_0^2 \cdot 10^{10} \times \text{tg}(180° - \varphi_1)]$
400*	0.8	43.5	3.8	13.5	2.6
412*	0.8	32	5.6	19.7	2.98

t, °C	x, mole fractions	$180^\circ - \varphi_1$	$n_0 \cdot 10^5$, mol/sec	$n_0^2 \cdot 10^{10} \times \operatorname{tg}(180^\circ - \varphi_1)$	$\ln [n_0^2 \cdot 10^{10} \times \operatorname{tg}(180^\circ - \varphi_1)]$
434	0.8	30	6.8	26.6	3.28
450	0.8	28.5	7.5	30.6	3.42
468	0.8	17	10.9	35.7	3.57
490	0.8	12.5	13.4	39.8	3.68
510	0.8	11	14.8	42.6	3.75
377	0.5	22	9	32.4	3.47
386	0.5	19.5	11	43.3	3.76
400	0.5	11.5	18	65	4.16

* Extrapolated.

1. The internal kinetic region is realized up to a temperature of 410°. In this region the activation energy is the greatest and amounts to 26.0 kcal/mol.
2. The internal diffusion region is observed at 430–460°, since here the activation energy is about 12 kcal/mol, i.e., close to one-half the value of the activation energy in the kinetic region.
3. The external diffusion region begins above 490°. The activation energy then decreases to the minimum value, equal to 3.3 kcal/mol.
4. Between 410 and 430° the activation energy passes through values from 26.0 to 12 kcal/mol, and, consequently, the reaction proceeds in the internal transition region.
5. Between 460 and 490° the reaction proceeds in the external transition region; the activation energy changes in this case from 12 to 3.3 kcal/mol.

Of course, the boundaries of each region are to some extent conventional, but such a division into regions is generally accepted for the convenience of analysis. Let us note that the presence of internal and external diffusion retardation is confirmed by experiments on crushed and sintered catalysts.

Thus, the graphical method of analyzing experimental curves has allowed us to determine the regions of occurrence and the observed activation energies without resorting to any analytical constructions. This method can also be used for determining other kinetic constants, as well as for quantitatively comparing the activity of various catalysts.

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CITED LITERATURE

1. G. M. Panchenkov, ZhFKh, **22**, 209 (1948); **26**, 454 (1952); Vestn. MGU, No. 6, 105 (1948).

2. G. M. Panchenkov, Scientific Notes of Moscow State University, Inorganic and Physical Chemistry, issue 53 (1955); G. M. Panchenkov, A. S. Kazanskaya, ZhFKh, **32**, 1779 (1958); I. M. Kolesnikov, Izv. Vyssh. uchebn. zaved., Neft' i gaz, No. 11, 77 (1958).

3. K. V. Topchieva, Sh. Battalova, G. M. Panchenkov, DAN, **78**, No. 3, 501 (1951); G. M. Panchenkov, E. P. Kuznetsova, DAN, **87**, No. 1, 65 (1952).

4. G. M. Panchenkov, V. Ya. Baranov, Izv. Vyssh. uchebn. zaved., Neft' i gaz, No. 6, 77 (1958).

5. K. V. Topchieva, G. M. Panchenkov, DAN, **74**, No. 6, 1109 (1950).

Note: Figure translations are in progress. See original paper for figures.