Adsorption kinetics from one-component gaseous phase*

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From an analysis of the kinetic isotherms of adsorption of organic substances on activated carbon Supersorbon measured in the temperature interval between melting point and boiling point it follows that the half-time of the process depends neither on temperature nor on the size of grains. The half-time was determined from the whole kinetic isotherm on the basis of the Trapnell equation and was found to be in a good agreement with the experimental value resulting from the kinetic isotherm. From the confrontation of activation energy with isosteric heat it may be concluded that the surface diffusion characterized by the activation energy equal to a half of isosteric heat can manifest itself at higher values of adsorption.

На основе анализа изотерм адсорбции органических веществ на активированном угле Суперсорбон, измеренных в температурном интервале между точкой плавления и точкой кипения, можно сделать вывод, что период полураспада не зависит от температуры и от размеров зерна. Период полураспада определялся из всей кинетической изотермы на основе уравнения Трапнелла и находился в хорошем согласии с экспериментально полученным значением, которое определялось из кинетической изотермы. Из сравнения энергии активации с изостерической теплотой вытекает, что при повышенных значениях адсорбции может иметь место поверхностная диффузия, которая характеризуется энергией активации, равной по величине половине изостерической теплоты.

The kinetic isotherm expressing the dependence of the adsorbed amount of substance on time at constant temperature and pressure gives an information on the character of the transport of adsorbate in the pores of sorbent. In the study of adsorption kinetics we investigated the transport rate as a function of the structure of adsorbent and the conditions under which the adsorption process took place. There is a great variety of possible conditions: the adsorption may occur in a system containing one-component or multicomponent gaseous phase, the adsorbent may consist of one substance or substance mixture, the adsorbent may be in a moving or fixed bed, *etc.* In our case, the investigated system consisted of a one-component gaseous phase and the adsorbent containing only one substance in the chemical sense. The adsorption kinetics can be measured by the following methods [1]:

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from the pressure change of adsorbate at a constant volume of apparatus, from the decrease in the volume of liquid adsorbate measured in a microburette, and gravimetrically at a constant pressure.

Theoretical

In kinetic investigations, the adsorbed amount a is a function of temperature T, pressure P, and time τ. The increase in the amount adsorbed may be expressed by the equation

$$da = \left(\frac{\partial a}{\partial \tau}\right)_{T,P} d\tau + \left(\frac{\partial a}{\partial P}\right)_{T,\tau} dP + \left(\frac{\partial a}{\partial T}\right)_{P,\tau} dT. \tag{1}$$

Assuming that the adsorbent is evacuated at the beginning of experiment, the integration of eqn (1) gives the expressions

a) for the kinetic isotherm

$$a = \int_0^\tau \left(\frac{\partial a}{\partial \tau}\right)_{T,P} d\tau, \tag{2}$$

b) for the isothermal isochrone

$$a = \int_0^P \left(\frac{\partial a}{\partial P}\right)_{T,\tau} dP, \tag{3}$$

c) for the isobaric isochrone

$$a = \int_0^T \left(\frac{\partial a}{\partial T}\right)_{P,\tau} dT. \tag{4}$$

For the limit $\tau \to \infty$ all these expressions imply equilibrium states, *i.e.* a) point on isotherm or isobar, b) equilibrium isotherm, c) equilibrium isobar.

In [2—4] the half-time was determined by means of the Trapnell equation which had been originally derived for chemisorption. This equation is, however, applicable also to physical adsorption as a correlation equation. It may be written

$$\frac{da}{d\tau} = w_0\left(1 - \frac{a}{a_r}\right)^2 \tag{5}$$

If eqn (5) is integrated for the initial condition (the sample evacuated at the beginning of experiment), it may be linearized in $\tau/a \sim \tau$ coordinates

$$\frac{\tau}{a} = \frac{1}{w_0} + \frac{\tau}{a_r}, \tag{6}$$

where w_0 is the initial rate $w_0 = a_r \beta$ and a_r is the equilibrium amount adsorbed under given conditions T, P. The half-time $\tau_{0.5} = 1/\beta$ was determined from the ratio of the intercept to the slope.

The dependence of diffusion coefficient on temperature may be expressed by the equation

$$\frac{\partial \ln D}{\partial T} = -\frac{\partial \ln \tau_{0.5}}{\partial T} = \frac{E}{RT^2}. \tag{7}$$

Assuming that the activation energy is constant in the investigated temperature interval, by the integration of this equation it is possible to calculate the activation energy as evident from the subsequent expression

$$\ln \left(\frac{D_2}{D_1}\right) = \ln \left[\frac{(\tau_{0.5})_1}{(\tau_{0.5})_2}\right] = -\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{8}$$

In [5, 6] the kinetic measurements have been confronted with equilibrium isotherms. From a few experimentally determined isotherms or from a characteristic curve we can determine the course of isosters and provided this course is linear, from the slope isosteric heat can be calculated. From the half-time *vs.* pressure relationship for equal values of pressure (as for isosters) the half-times can be determined. The half-time is inversely proportional to the diffusion coefficient so that the activation energy may also be determined from the temperature dependence of half-times (see eqn (8)) and confronted with isosteric heats.

For the calculation of diffusion coefficient it is possible to use the relationship between the relative adsorption (a/a_r) and the dimensionless Fourier criterion Fo $= D \tau/R^2$, where D is the diffusion coefficient, R is the size of grain, and τ is time.

The monograph [1] contains a critical compilation of the formulae for the calculation of diffusion coefficients by means of half-times for different geometrical shapes of grains.

From the kinetic isotherms measured at different temperatures and pressures we may obtain not only the data for the characterization of the transport mechanism of adsorbate in pores but also the equilibrium data. By using the terminal isotherms we can draw the characteristic curve which gives the relationship between adsorption potential ε and adsorption volume W or the relationship between ε and the

Table 1

Formulae for the calculation of effective diffusion coefficients by means of half-times

Geometrical shape of grain	Effective diffusion coefficient D_e	Accuracy of the calculation of D_e %
Cylinder[a]	$1.96\ L^2/(\pi^2\ \tau_{0.5})$	0.1
Cylinder[b]	$k\ R^2/(\pi^2\ \tau_{0.5})$	1
Sphere	$0.308\ R^2/(\pi^2\ \tau_{0.5})$	—

a) Adsorbate enters the grain only through one base of the cylinder.
b) The value of the constant k for different ratios of the length L and the radius R.

L/R	1	2	4	∞
k	0.168	0.318	0.450	0.599

adsorbed amount referred to the expansion factor $\omega = T_r/(z\,P_r)$ where T_r is reduced temperature, P_r is reduced pressure, and z is the compressibility factor.

The characteristic curve may be drawn not only by means of isotherms but also on the basis of isosters or isobars. The isothermal or isobaric isochrones can be also used for the construction of the characteristic curve. In [7] the assertion presented in [8—10] was confirmed that the half-time does not depend on temperature provided the kinetic measurements are performed at temperatures below the normal boiling point of adsorbate. If the measurements are performed at temperatures above the boiling point, the half-time depends on pressure at lower temperatures while it is independent of pressure at higher temperatures.

Results and discussion

For n-pentane and n-hexane the dependence of half-time on pressure is governed by the following equation (at temperatures below the boiling point)

$$\tau_{0.5} = K\,P^{-n}, \qquad (9)$$

where K and n are constants. By inserting the logarithms and differentiating eqn (9) with respect to temperature at a constant amount adsorbed, we obtain the following relation between activation energy and isosteric heat

$$E = n\,Q_{iso}. \qquad (10)$$

If it is not possible to express the relationship between half-time and pressure in simple terms, the correlation of isosteric heats with activation energy may be determined graphically. For equal pressures as those of individual isosters we read the half-times at corresponding temperatures. The activation energy is then to be calculated according to eqn (8).

The kinetic isotherms measured at different temperatures and pressures enable us to correlate the kinetic data in terms of isothermal and isobaric isochrones. This correlation makes it possible to determine the course of kinetic isotherm under different conditions. According to eqn (4), the adsorbed amount—temperature
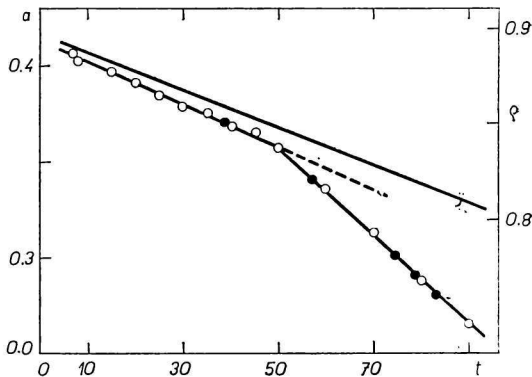
Fig. 1. The adsorbed isobaric equilibrium amount as a function of temperature.
Black points denote the values of adsorption determined from isosters, white points denote the experimental values.
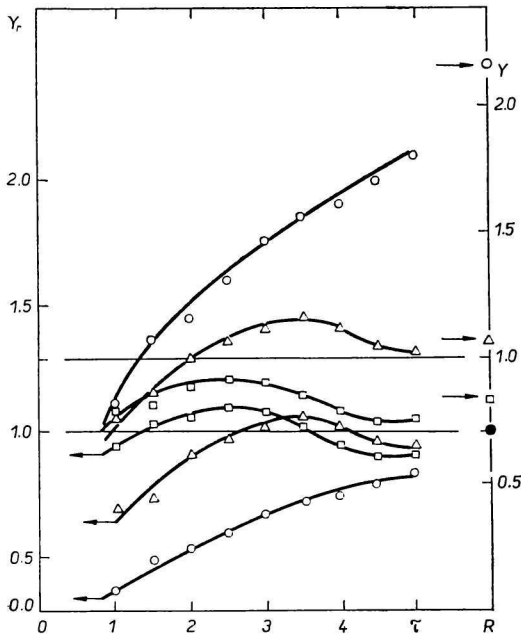
Fig. 2. The slopes of isobaric isochrones as a function of time.
$$Y_r = (da/dt)_\tau/(da/dt)_r,$$
$$Y = (da/dt)_\tau/(d\varrho/dt).$$
τ is time in minutes and R designates equilibrium.

relationships at a constant pressure and a given time moment were drawn. In the investigation of the system benzene—Supersorbon in the temperature interval between 7 and 90°C a bending was revealed at about 50°C which appeared not only on the equilibrium isobar (Fig. 1) but also on individual isochrones. Similar bendings were described in [7, 9].

Besides the equilibrium isobar Fig. 1 shows the relationship between the density of liquid adsorbate and temperature expressed in the same modulus as used for the relationship between the adsorbed amount and temperature. The black points denote the values of adsorption determined from isosters. Fig. 2 shows the slopes of isobaric isochrones referred to the value of the slope of equilibrium isobar $Y_r = (da/dt)_\tau/(da/dt)_r$ for cyclohexane ($\square$), in the temperature interval 0—50°C, for benzene ($\triangle$), 0—50°C, the slope as a function of time τ ($\bigcirc$), between 50—90°C. Fig. 2 also presents the slopes of isobaric isochrones referred to the value of the slope of the dependence of the density of liquid adsorbate on time

$$Y = (da/dt)_\tau/(d\varrho/dt).$$

The denotation of the time interval and adsorbates is the same as the one used for Y_r. As obvious from Fig. 2, the course of the dependence Y_r vs. τ in the temperature interval 0—50°C is already in the first minutes close to the value $Y_r = 1$ (black point) for both benzene and cyclohexane. For benzene, the course of Y_r is gradual in the temperature interval 50—90°C. The dependence of Y on time is analogous to that of Y_r, but for benzene the ratio of the slopes attains the value of about 2 in the temperature interval 50—90°C while it reaches only a half this value in the temperature interval 0—50°C. For benzene and cyclohexane in the tem-

perature interval 0—50°C the temperature change in the adsorbed equilibrium amount equals approximately to the temperature change of normal liquid.

Fig. 3 shows the kinetic isotherm of *n*-heptane on activated carbon Supersorbon. The black point indicates the half-time determined from the Trapnell equation. The halved point expresses the value of the half-time read from the kinetic isotherm. As obvious from Fig. 3, these values of half-times are in good agreement.
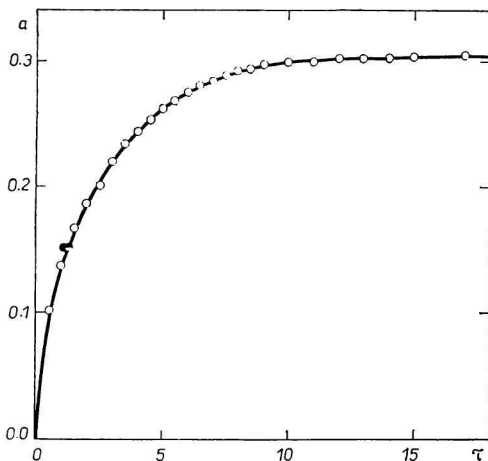

Fig. 3. Kinetic isotherm of *n*-heptane on activated carbon Supersorbon.

$P = 2.7$ torr, $t = 0$°C.

a is the adsorbed amount in grams per 1 gram of adsorbent, τ is time in minutes.

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