Isosteric adsorption heats in correlation with activation energy of diffusion*

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From the dependence of diffusion coefficients on temperature it is possible to calculate the activation energy of transfer of the adsorbate in pores. For small values of the adsorption of propane on active carbon Supersorbon the activation energy of transfer is equal to the adsorption isosteric heat. At higher adsorption values, even the surface diffusion may play a role, *i.e.* the activation energy is approximately equal to a half of the isosteric heat. For pentane, hexane, heptane, benzene, and cyclohexane the activation energy of transfer is equal to a half of the isosteric heat.

На основе температурной зависимости диффузионных коэффициентов можно рассчитать энергию активации переноса адсорбированного вещества в порах. При малой адсорбции пропана на активированном угле Суперсорбон энергия активации переноса равна изостерической теплоте адсорбции, а при высокой адсорбции может иметь место также поверхностная диффузия, т. е. энергия активации равна приблизительно половине изостерической теплоты. В случае пентана, гексана, гептана, бензола и циклогексана энергия активации переноса равна половине изостерической теплоты.

Isosteric heats can be determined directly from the measured isosters or indirectly from several measured isotherms either graphically or by calculation [1, 2]. In the last case, two variants are possible. The first one consists in expressing each isotherm by a mathematical relation from which the pressure for a given amount adsorbed can be determined with satisfactory accuracy. Then the course of isosters may be determined from particular pressures. The other variant is based on the existence of a characteristic curve independent of temperature. The shortcoming of this method consists in the fact that it is not always possible to be successful in expressing the characteristic curve by a simple mathematical expression in the entire range of temperatures and pressures. As shown in some papers, the course of isosters is nonlinear if the values of adsorption are higher. This fact was verified both by a direct measurement of the isosters [3, 4] and a calculation of the course of isosters on the basis of the characteristic curve [1].

Theory

If the diffusion of a sorbing gas takes place, the temperature dependence of the diffusion coefficient may be expressed by the following equation

$$D_e = D_0 \exp\left(\frac{-E}{RT}\right). \tag{1}$$

Provided the activation energy in the temperature interval from T_1 to T_2 is constant, it is possible to write

$$E = 2.303 \frac{RT_1 T_2}{T_2 - T_1} \log \frac{D_2}{D_1}. \tag{2}$$

Since the diffusion coefficient is inversely proportional to the half-time, the activation energy may be expressed by the following equation

$$E = 2.303 \frac{RT_1 T_2}{T_2 - T_1} \log \frac{(\tau_{0.5})_1}{(\tau_{0.5})_2}. \tag{3}$$

According to *Timofeev* [5] the character of the activation energy in a sorption process is dependent on the structure of adsorbent. Equation (1) may be obtained for different mechanisms of gas sorption. Provided the transfer is controlled by the Knudsen diffusion, it holds $D_e = D_k/(1 + \Gamma)$. In most cases $\Gamma \gg 1$, hence in the first approximation we write $D_e = D_k/\Gamma$ The temperature dependence of the Henry coefficient is described by the relationship $\Gamma = \Gamma_0 \exp(\Delta H/RT)$. Therefore the diffusion coefficient can be expressed by equation

$$D_e = \frac{D_k}{\Gamma_0} \exp\left(\frac{-\Delta H}{RT}\right). \tag{4}$$

ΔH being the differential heat of adsorption. If the temperature dependence of D_k and Γ_0 may be neglected, eqn (4) assumes a form analogous to that of eqn (1).

In a case of the surface diffusion, the dependence of the diffusion coefficient on temperature is analogous to eqn (1) and the activation energy is smaller than the adsorption heat. At high relative pressures the polymolecular adsorption and capillary condensation take place and the transfer af adsorbate in sorbing pores is characterized by the flow of the liquid adsorbate. For the flow of viscous liquids an activation energy is also required for overcoming the cohesive forces between the molecules. The activation energy of the viscous flow of liquids is approximately equal to one third or one quater of the evaporation heat.

According to *de Boer* [6], the character of the diffusion in capillaries may be explained by three mechanisms:

1. The molecules can collide with capillary walls and immediately rebound from them (the cosine law is valid), collide anew, and so on. In this case the activation energy of the diffusion process is equal to zero.

2. The molecules collide with capillary walls and remain in contact with them for a space of time τ', evaporate, collide again, and so on. In this case, the activation energy of the diffusion process is equal to the heat of adsorption.

3. The molecules can move along capillary walls for a sufficiently long space of time τ'' For these "jumping" molecules the activation energy is much smaller than the heat of adsorption.

From the relationship between the adsorption (ethane and propane on active carbon) and temperature, the activation energy was found to be approximately equal to 3 kcal/mol which represents about a half of the heat of adsorption [6].

Experimental

The kinetic isotherms were measured in a greaseless adsorption apparatus [7] by gravimetric method. The quartz spiral had 50 coils of 25 mm in diameter and its sensitivity was 0.7 mg mm^{-1}. The sample of adsorbent was evacuated at the pressure of 1×10^{-6} torr and at 350°C for 5 hrs. The kinetic isotherms were measured for active carbon Supersorbon which is included among active carbons of the first structural type according to Dubinin's classification [8—10]. The kinetic isotherms were correlated
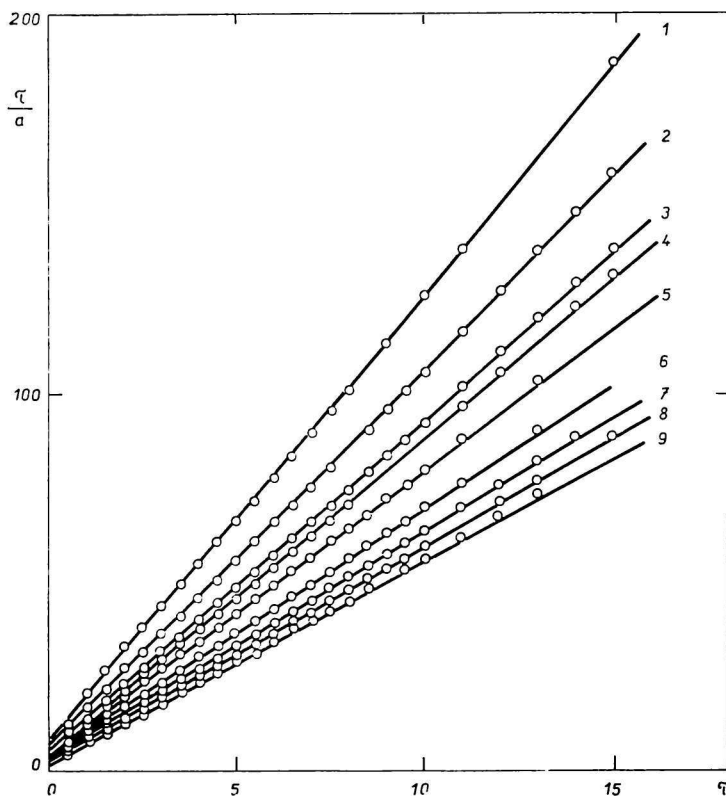

Fig. 1. Kinetic isotherms of propane at 30°C on active carbon Supersorbon at various pressures (in torr).
1. 15.5; *2.* 25.7; *3.* 40.7; *4.* 46.7; *5.* 66.5; *6.* 117.2; *7.* 177.8; *8.* 252.4; *9.* 335.5.
τ = time in minutes, a = g/g.

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by means of the Trapnell eqn [11] which had been originally derived for chemisorption. The Trapnell equation

$$\frac{da}{d\tau} = W_0 \left(1 - \frac{a}{a_e}\right)^2 \qquad t, p = \text{const} \tag{5}$$

was integrated for the boundary conditions $a = 0$, $\tau = 0$, $a = a$, $\tau = \tau$ at constant temperature and pressure, where a is the adsorbed amount at the time moment τ, a_e is the limiting (equilibrium) amount adsorbed at a given temperature and pressure, W_0 is the initial rate while $W_0 = a_e \beta$, and β is the kinetic potential. The linear form of eqn (5) integrated under these conditions is

$$\frac{\tau}{a} = \frac{1}{W_0} + \frac{\tau}{a_e}, \qquad t, p = \text{const} \tag{6}$$

and may be written in the form

$$\frac{\tau_i}{a_i} = K_{(p)} \tau_i + M_{(p)}. \tag{7}$$

At constant pressure and temperature $K_{(p)}$ and $M_{(p)}$ are constants; generally, however, they are a function of pressure at constant temperature. The half-time (*i.e.* the time necessary for one half of the equilibrium amount to get adsorbed) may be calculated from the ratio of intercept to slope according to eqn (6). The kinetic isotherms of propane on active carbon Supersorbon at 30°C are represented in Fig. 1 by the linear form of
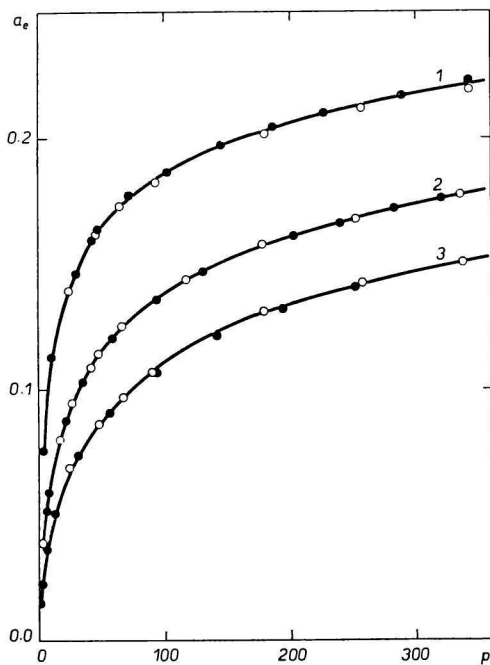

Fig. 2. Isotherms of propane on active carbon Supersorbon.

1. 0°C; *2.* 30°C; *3.* 50°C.

● Points obtained by the measurement of equilibrium isotherms; ○ terminal points of kinetic isotherms.

$a_e = $ g/g, $p = $ torr.

the Trapnell equation. The equilibrium isotherms of propane from which the isosteric heats were estimated are shown in Fig. 2. By means of the Trapnell equation the half-times were calculated from the course of the kinetic isotherms. The dependence of half-times on temperature and pressure was used to the graphical determination of the half--times for propane at given temperatures and pressures. On the basis of the values obtained the course of isosters was determined. The results are presented in Table 1.

Table 1

Activation energy E and isosteric heat Q_{iso} of propane as a function of the equilibrium adsorbed amount a_e

a_e g/g	Q_{iso} kcal/mol	E kcal/mol	a_e g/g	Q_{iso} kcal/mol	E kcal/mol
0.05	7.50	7.38	0.11	8.36	3.08
0.06	7.67	6.53	0.12	8.23	2.80
0.07	7.93	7.73	0.13	8.30	3.53
0.08	8.47	4.85	0.14	8.39	3.40
0.09	8.42	4.24	0.15	8.15	3.29
0.10	8.48	3.63			

The dependence of the half-time on pressure was expressed for n-pentane and n-hexane at different temperatures by the following relation

$$\tau_{0.5} = k\, p^{-n}, \tag{8}$$

where $\tau_{0.5}$ is the half-time and k, n are constants. By taking the logarithms and differentiating eqn (8) with respect to temperature at constant adsorbed amount and constant adsorbent surface, we obtain

$$\frac{\partial \ln \tau_{0.5}}{\partial T} = -n\, \frac{\partial \ln p}{\partial T}. \tag{9}$$

The dependence of diffusion coefficient on temperature obeys the subsequent relation (see eqns *(1—3)*)

$$\frac{\partial \ln D_e}{\partial T} = -\frac{\partial \ln \tau_{0.5}}{\partial T} = \frac{E}{RT^2}. \tag{10}$$

The isosteric adsorption heat is defined in literature by the equation

$$\frac{\partial \ln p}{\partial T} = \frac{Q_{iso}}{RT^2}. \tag{11}$$

By combining eqns *(9—11)* we obtain the relationship between activation energy and isosteric adsorption heat

$$E = n\, Q_{iso}. \tag{12}$$

Discussion

For a given amount of propane adsorbed (Table 1) the pressures corresponding to individual isosters were read from equilibrium isotherms. From the course of these isosters the isosteric heats were calculated.

The half-times were read graphically from their pressure dependences for the same temperatures and pressures as for isosters. The activation energy was determined from the logarithmic dependence of half-times on reciprocal temperature. For low values of adsorption the activation energy is equal to the adsorption heat (Table 1) while for higher adsorption the activation energy decreases. This phenomenon was also observed by other authors. On the basis of the relation between adsorption (ethane and propane on carbon) and temperature it was found that the activation energy equals approximately to 3 kcal/mol which represents about a half of the adsorption heat [6]. The constants in eqn (8) are: for n-hexane $n = 0.53 \pm 0.02$, $\log k = 2.14 \pm 0.02$, temperatures 0, 30, and 50°C; for n-pentane $n = 0.45 \pm 0.02$, $\log k = 2.14 \pm 0.03$, temperatures 0, 10, 20, 30, 40, 50, and 120°C. If $n = 0.5$, from eqn (12) it ensues that the activation energy for the transfer of the adsorbate equals to one half of the isosteric heat. The decrease in the activation energy to half a value of the isosteric heat might be due to the existence of surface diffusion [5, 6].

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