

KINETICS OF ADSORPTION. III.*

CORRELATION OF KINETIC ISOTHERMS
IN AN ISOTHERMAL SPACE DIAGRAM

Z. SEDLÁČEK

*Department of Physical Chemistry,
Institute of Chemical Technology, Prague 6*

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An isothermal space diagram is used for correlation of kinetic data; coordinates are the adsorbed amount, pressure and time. The plane of constant time and temperature, perpendicular to the planes containing the kinetic isotherms, contains the dependence of the adsorbed amount on pressure. This dependence is correlated by an equation whose independent variable is the same as in the equilibrium adsorption isotherm. The mechanism of the transfer of propane on active charcoal "Supersorbon" is characterized by Knudsen diffusion; at higher surface coverages also surface diffusion probably plays a role.

The adsorbed amount, a , is a function of temperature, T , pressure, P , and time, τ (ref.¹). If one of these variables is maintained constant, the dependence of the adsorbed amount on time and pressure can be depicted in a three-dimensional diagram $a = f(P, \tau)$. If, in addition, also another variable is maintained constant, a plane is formed in the diagram. This plane is parallel to the basic plane and is shifted with respect to the latter by a constant value². The kinetic isotherms $a = f(\tau)$ lie in the planes that are perpendicular to the pressure axis and intersect the latter in a point corresponding to the pressure at which they were measured. A plane perpendicular to the mentioned planes gives the dependences of the adsorbed amount on pressure at a given time and has therefore the same coordinate as the equilibrium adsorption isotherm. In a binary system propane-active carbon "Supersorbon", equilibrium data measured at 30 and 50°C can be correlated with a satisfactory accuracy on the basis of the Dubinin equation for adsorbents of the first structural type near the critical temperature. Half-times which are inversely proportional to diffusion coefficients can be calculated from the individual kinetic isotherms on the basis of the Trapnell equation^{2,3}; their temperature dependence gives the activation energy for the same pressures for which isosteric heats are calculated.

THEORETICAL

The active carbon "Supersorbon" belongs to the first structural type after Dubinin's classification of active carbons⁴⁻⁶. In the program for National Elliott 803 B type

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computer⁷, the Dubinin equation for adsorbents of the first structural type at temperatures near the critical one or higher was used to calculate the equilibrium adsorption isotherm of propane on the mentioned adsorbent. Experimental values must be measured at a temperature $T > 0.8 T_k$ or better $T \geq T_k$, where T_k denotes the critical temperature of the adsorbate. The linearized form of the mentioned equation in the mentioned temperature range is

$$\log a_e = \log (W_0/b) - (0.43 BT^2/\beta^2) \log^2 (P_k T^2/(PT_k^2)), \quad (1)$$

where a_e denotes the equilibrium adsorbed amount at temperature T and pressure P , W_0 limiting volume of adsorption space, b constant of the van der Waals equation ($= RT_k/(8P_k)$), P_k critical pressure, B sorption constant of the adsorbent and β affinity coefficient.

Isochrons defined at constant temperature can be depicted together with kinetic isotherms in an isothermal space diagram, where the coordinates are the adsorbed amount, pressure and time². The adsorbed amount was correlated with pressure at a given time on the basis of the equation

$$\log a = \log (\bar{W}_{0i}/b) - (0.43\bar{B}T^2/\beta^2) \log^2 (P_k T^2/(PT_k^2)), \quad (2)$$

whose independent variable is the same as in (1); a means adsorbed amount at a given time at constant P and T , \bar{W}_{0i} limiting volume of the adsorption space for i -th isochron, \bar{B} constant characterizing the form of the isochron. Other symbols have the same meaning as in Eq. (1). The kinetic isotherms can be expressed by the Trapnell equation^{3,8} from which the half-time can be determined, which is inversely proportional to the diffusion coefficient. The effective diffusion coefficient D_e can be estimated⁹ from the equation $D_e = kR^2/(\pi^2\tau_{1/2})$, where k is a constant depending on the geometry of the adsorbed grain, R its radius, π Ludolf number and $\tau_{1/2}$ half-time. The dependence of D_e on temperature enables us to calculate the activation energy of transfer of the adsorbate. Assuming that the activation energy is constant in the given temperature interval we can calculate it from the equation

$$E = \frac{2.303RT_1T_2}{T_1 - T_2} \log (D_1/D_2), \quad (3)$$

or from

$$E = \frac{2.303RT_1T_2}{T_1 - T_2} \log (\tau_{1/2}^2/T_1\tau_{1/2}^2) \quad (4)$$

where R denotes gas constant, D_1 and D_2 effective diffusion coefficients at temperatures T_1 and T_2 .

EXPERIMENTAL

The kinetic isotherm is experimentally best accessible since it expresses the dependence of adsorbed amount on time at constant pressure and temperature. It can be determined in a sorption apparatus in which the sample adsorbent hangs on a sensitive spiral balance. The adsorbate pressure can be kept constant by reservoirs of large volume³ or by a cryostat maintaining constant temperature of the liquid adsorbate^{10,11}. We used in this work reservoirs of a volume of 33 l.

RESULTS

Of the 24 kinetic isotherms of propane measured at 0; 30 and 50°C, in Fig. 1 are shown those at 30°C and at various pressures.

In contrast to the usual definition of an isochron¹, we define it at constant temperature and time. This enables us to obtain from kinetic isotherms at chosen time intervals the isochronous dependence of the adsorbed amount on pressure shown in Fig. 2, where the time intervals correspond to Fig. 1. The region of higher pressures is in Fig. 3. The curves joining the isochronous points were calculated in the whole pressure range in which the kinetic isotherms were measured, *i.e.* from 2.4 to 335 Torr (Fig. 3). White circle denotes the end point of the kinetic isotherms, *i.e.* the limiting (equilibrium) adsorbed amount at a given temperature and pressure. Black circles denote the equilibrium adsorption isotherm obtained by measurement.

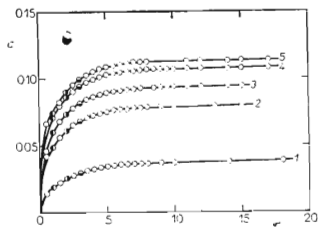


FIG. 1

Kinetic Isotherms for Propane on Active Carbon Supersorbent at 30°C

Pressure values: 1 2.4; 2 15.5; 3 25.7; 4 40.7; 5 46.7 Torr. Grain of cylindrical shape, 6 mm in diameter and in height. 1st minute ○, 2nd minute ●, 3rd minute ◐; *a* in g/g, τ in min.

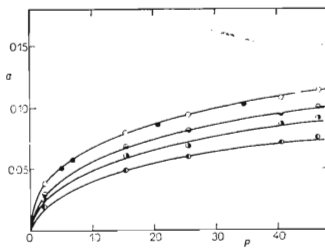


FIG. 2

Isochronous and Equilibrium Dependences of Adsorbed Amount of Propane on Pressure at 30°C

1st minute ○, 2nd minute ●, 3rd minute ◐, equilibrium from end points of kinetic isotherms ○, equilibrium adsorption isotherm ●; *a* in g/g, *P* in Torr.

The isochronous dependence of the adsorbed amount on pressure is analogous to the dependence of the equilibrium adsorbed amount on pressure, *i.e.* to the equilibrium adsorption isotherm. Both these types of dependences are in Fig. 4 expressed in linear coordinates of the Dubinin equation for adsorbents of the first structural type in the region of critical temperature and above. The numerical values on the axis of the independent variable are the same (measurements were performed at constant temperature and pressure) as for the equilibrium adsorption isotherm obtained from the end points of the kinetic isotherms. On the axis of the dependent

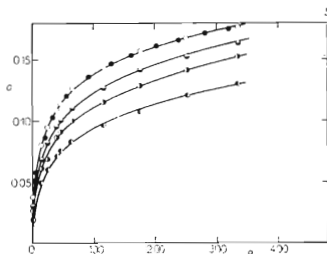


FIG. 3

Isochronous and Equilibrium Dependences of Adsorbed Amount of Propane on Pressure at 30°C
1st minute \odot , 2nd minute \ominus , 3rd minute $\omin�$, equilibrium from end points of kinetic isotherms \circ , equilibrium adsorption isotherm \bullet ; a in g/g, P in Torr.

TABLE I

Results of Correlation Based on Equation (1)

Eq. (1)	W_0/b	Slope of straight line
End points of kinetic isotherms (10 points \circ)	0.270	-0.0535 ± 0.0005
Equil. adsorption isotherm (14 points \bullet)	0.269	-0.0538 ± 0.0003
All experimental points (23 points)	0.269	-0.0536 ± 0.0003

variable is plotted the logarithm of the adsorbed amount at a given time; this value for $\tau \rightarrow \infty$ is equal to that determined from the equilibrium adsorption isotherm.

TABLE II

Results of Correlation for Isochrons Defined at Constant Temperature and Time; Equation (2)

Eq. (2)	$W_{0,i}/b^a$	Slope of i -th isochron
1st minute ●	0.215	-0.066 ± 0.001
2nd minute ●	0.243	-0.062 ± 0.001
3rd minute ●	0.257	-0.0587 ± 0.0006
4th minute ○	0.263	-0.0568 ± 0.0006
$\tau \rightarrow \infty$	0.270	-0.0535 ± 0.0005

^a Correlation based always on 10 points; $i = 1, 2, 3, 4, \infty$.

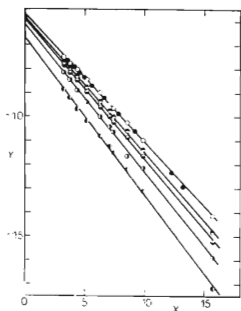


FIG. 4

Isochrons and Equilibrium Data for Propane on Active Carbon Supersorbon at 30°C in Linear Coordinates

$Y = \log a$ (for isochrons — Eq. (2)); $Y = \log a_e$ (for equilibrium data — Eq. (1)); $X = \log^2(P_k T^2 / P T_k^2)$; 1st minute ●, 2nd minute ●, 3rd minute ●, 4th minute ●; end point of kinetic isotherm (equilibrium) ○, point of equilibrium isotherm ●.

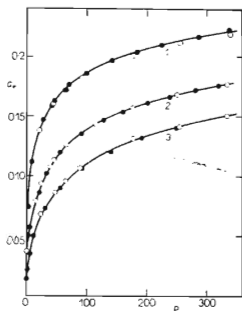


FIG. 5

Equilibrium Adsorption Isotherm for Propane

Temperature: 1 0°; 2 30°; 3 50°C; a_e in g/g, P in Torr. End point of kinetic isotherm ○, point of equilibrium isotherm ●.

In Table I are shown the results of correlation of experimental data for propane at 30°C based on Eq. (1). The correlation of isochronous data is based on Eq. (2) which differs from (1) in that the adsorbed amount values at a given time and at various pressures were substituted for a_e ; the results are summarized in Table II. It is seen that the isochron defined at constant temperature and time is suitable for correlation of kinetic data obtained from kinetic isotherms.

In Fig. 5 are shown the equilibrium adsorption isotherms at 0, 30 and 50°C. From these in the range of the adsorbed amount 0.05–0.15 g, isosters were constructed and the isosteric heats were calculated. Half-times for the kinetic isotherms were calculated from the Trapnell equation. From the dependence of the half-time on pressure, half-times at the given temperatures were determined for the same pressures as with the isosters.

DISCUSSION

The mechanism of transfer of the adsorbed substance can be different depending on the structure of the adsorbent and on experimental conditions. The transfer of the adsorptive can proceed as surface diffusion (migration of molecules along the surface). The character of the gas flow in the pores depends on the mean free path of molecules, λ , and on the pore radius, r . For $\lambda/r \ll 1$ we have a viscous gas flow characterized by collisions of molecules with one another. In smaller pores with radii below 10^{-6} cm there is no viscous flow at 1 atm. pressure. For $\lambda/r \gg 1$ collisions of molecules occur only with pore walls resulting in a different character of the gas flow in the pores. Molecules colliding with pore walls are reflected into different directions. Every substance is adsorbed to a certain degree, its molecules are after collision with pore walls in the adsorbed state for a certain time. Owing to thermal

TABLE III

Activation Energy E and Isosteric Heats Q_{iso} for Propane as Function of 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	0.10	8.48	3.63
0.06	7.67	6.53	0.11	8.36	3.08
0.07	7.93	5.73	0.12	8.23	2.80
0.08	8.47	4.85	0.13	8.30	3.53
0.09	8.42	4.24	0.14	8.39	3.40
			0.15	8.15	3.29

motion the molecules are desorbed, no direction of their motion being preferred (molecular flow). Dacey and Fendley¹² studied the influence of diffusion of hydrogen, argon, methane and neon on a saran type carbon which has no large pores. They concluded from their experiments that in such small pores the viscous flow at atmospheric pressure is not possible. Their carbon had a specific surface of $680 \text{ m}^2/\text{g}$, porosity $0.56 \text{ cm}^3/\text{cm}^3$ and mean pore radius 16.5 \AA . The authors indicated the activation energy of transfer, E , to be 4790 cal/mol for methane and 3820 cal/mol for argon. The transfer of adsorbate proceeds prevailingly by Knudsen diffusion while surface diffusion represents only 11.5% of the total flow of the adsorbate. After de Boer¹³ the character of diffusion in capillaries can be elucidated by three mechanisms: 1. Molecules can collide with the capillary walls and immediately reflect from them (the cosine law holds), collide anew and so on. In this case the activation energy of the diffusion process is equal to zero. 2. Molecules collide with the capillary walls and remain in contact with them for a time τ' , evaporate, collide anew and so on. The activation energy of the diffusion process is equal to the heat of adsorption. 3. Molecules can move along the capillary walls during a sufficiently long time interval τ'' . In this case of "jumping" molecules the activation energy is much smaller than the heat of adsorption. Barrer and Strachan¹⁴ measured the adsorption isotherms and diffusion rate of helium, neon, hydrogen, nitrogen, argon and krypton on "Carbolac" carbon black. The rod-shaped samples were $3-5 \text{ cm}$ in length and 0.5 cm in diameter. They found that the activation energy for argon, nitrogen and krypton equals to $0.53-0.62$ times the adsorption heat while for helium, neon and hydrogen it is approximately equal to RT .

The activation energy of transfer of the adsorbate calculated from Eq. (4) is given in Table III. It is seen that at small surface coverages the activation energy is equal to the isosteric heat and decreases with increasing surface coverage. The transfer of adsorbate in the pores proceeds prevailingly by Knudsen diffusion if the activation energy is equal to about 0.8 times the isosteric heat¹¹; if it is smaller then also the surface diffusion plays a role^{11,13,14}. In reference¹³, the activation energy for adsorption of propane on active carbon is given as 3 kcal/mol representing about one half of the heat of adsorption.

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