

KINETICS OF ADSORPTION. IV.*

CORRELATION OF KINETIC DATA FOR n-PENTANE AND n-HEXANE BY MEANS OF AN EQUATION WHOSE INDEPENDENT VARIABLE IS THE SAME AS THAT FOR EQUILIBRIUM ADSORPTION ISOTHERM

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Equations have been used for correlation of the isothermal isochrone which in limiting case express the equilibrium adsorption isotherm. The form of the correlation equation for the isothermal isochrone depends on the adsorbent and adsorbate. In the binary system propane-active carbon "Supersorbon", the isothermal isochrones and equilibrium isotherms were correlated by equations whose independent variable coordinate was in the region near the critical temperature and in this work for temperatures satisfying the condition $T \leq 0.8T_k$ using the Dubinin equation for adsorbents of the first structural type. From the kinetic data obtained it is evident that for the case of n-pentane and n-hexane the surface diffusion can take place.

When bringing an adsorbed gas into contact with a solid phase which is able to adsorb it on its surface, then in the close system the number of molecules in the gas phase decreases and the number of molecules attached to the surface of the adsorbent increases. The number of molecules N that vanish from the gas phase is a function of temperature T , pressure P , and time τ (ref.^{1,2}). An analytical expression of this function for all three independent variables is rather difficult. For this reason we are forced, as a rule, into studying some of simpler functions when treating the kinetic data. The kinetic isotherm $N = F_1(\tau)$ at constant T , P is experimentally most easily accessible. In addition it may be the kinetic isoster $\tau = F_2(T)$ at constant N , P and isochrone $N = F_3(T)$ at constant τ , P . Using the general expression $N = F(T, P, \tau)$, we can define a further function $N = F_4(P)$ at constant T , τ , i.e. the isothermal isochrone³.

THEORETICAL

In case when during the adsorption the dissociation does not take place, the number of mol that disappeared from the gas phase is equal to the number of adsorbed mol. An increase in the adsorbed amount a as a function of temperature T , pressure P and time τ may be expressed by the equation

$$da = (\partial a / \partial \tau)_{T,P} d\tau + (\partial a / \partial P)_{T,\tau} dP + (\partial a / \partial T)_{P,\tau} dT. \quad (1)$$

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If two of the variables are maintained constant and the sample of the adsorbent is evacuated at the beginning of the experiment, then from Eq. (1) we can write the expression for kinetic isotherm

$$a = \int_0^{\tau} (\partial a / \partial \tau)_{T,P} d\tau, \quad (T, P) \quad (2)$$

which for $\tau \rightarrow \infty$ expresses the equilibrium adsorbed amount at the given pressure P , *i.e.* one point of the equilibrium isotherm. The isothermal isochrone is defined by the equation

$$a = \int_0^P (\partial a / \partial P)_{T,\tau} dP. \quad (T, \tau) \quad (3)$$

For $\tau \rightarrow \infty$ Eq. (3) expresses the equilibrium adsorption isotherm. The isobaric isochrone is defined by the equation

$$a = \int_0^T (\partial a / \partial T)_{P,\tau} dT, \quad (P, \tau) \quad (4)$$

which for $\tau \rightarrow \infty$ expresses the equilibrium isobar. In the paper³ the equations were used for the correlation of kinetic data for isothermal isochrones whose independent variable coordinate was numerically the same as that of the equilibrium adsorption isotherms determined from end points of kinetic isotherms. For correlating the isothermal isochrones, the relations with coordinates $P/a - P$, $X/[a(1 - X)] - X$ were used, where a is the adsorbed amount in a given time, P equilibrium pressure at which the kinetic isotherm was measured, $X = P/P_0$ relative pressure, P_0 saturated vapour pressure at temperature T . For $\tau \rightarrow \infty$, a_∞ represents the equilibrium adsorbed amount and the relations given express Langmuir's equation and the BET equation. When correlating the kinetic data by means of isothermal isochrones with coordinates $P/a - P$, we had to determine the pressure range from equilibrium isotherms, for the equilibrium adsorption isotherm could not be correlated by Langmuir's equation in the whole pressure interval because the active carbon "Supersorbon" belongs to the heterogeneous adsorbents. It was found³ that adsorption isotherms of *n*-butane on the active charcoal "Supersorbon" may be divided into two pressure ranges, from 0.0 to 0.1 of relative pressure and from 0.1 to about 1. For the given pressure regions, the equations can be used that have the same independent variable coordinate as Langmuir's isotherm but different constants. The equation of the BET isotherm may be used for correlation in the relative pressure interval from 0.05 to 0.35.

In order that we might correlate kinetic data by means of isothermal isochrones in whole pressure range, an equation was used whose independent variable coordinate was again the same as that for the equilibrium adsorption isotherm constructed from end points of kinetic isotherm. In the paper¹, Eq. (3) defining the isothermal isochrone was expressed by an analytical expression that for $\tau \rightarrow \infty$ turns into the equilibrium adsorption isotherm. For kinetic isotherm of propane measured at the temperature of 30 and 50°C, *i.e.* in the critical temperature region, the equation with variables $\log a - \log^2 [P_k T^2 / (PT_k^2)]$ was used, where a is the adsorbed amount in a given time P , is equilibrium pressure at which the kinetic isotherm is measured, P_k critical pressure, T_k critical temperature, T temperature at which measurements are made. Coordinates for correlations were chosen with respect to the adsorbate,

temperature interval of measurements and the condition (Eq.(3)) that for $\tau \rightarrow \infty$ the equation used must express the equilibrium adsorption isotherm. On the basis of measurements of the adsorption of carbon disulphide⁴ and trichloroethylene⁵ on active carbon "Supersorbon" it was found that equilibrium adsorption data conformed to the Dubinin equation for adsorbents of the first structural type with a satisfactory accuracy. For correlation of the kinetic data of n-pentane and n-hexane measured at the temperature satisfying the condition $T \leq 0.8T_k$, the equation must be used for the isothermal isochrone (Eq. (3)) which in time $\tau \rightarrow \infty$ expresses the equilibrium adsorption isotherm. With regard to this fact we can express Eq. (3) for these adsorbent and adsorbates at temperatures below $0.8T_k$ by an equation whose linear form is

$$\log a = \log (W_{0i}\varrho) - 0.43B_i T^2 / \beta^2 \cdot [\log (P_0/P)]^2, \quad (T, \tau_i) \quad (5)$$

which gives for $\tau \rightarrow \infty$ the equilibrium adsorption isotherm whose linear form is

$$\log a_e = \log (W_0\varrho) - 0.43BT^2 / \beta^2 \cdot [\log (P_0/P)]^2, \quad (6)$$

where ϱ is density of the liquid adsorbate (g/cm^3), B_i constant characterizing the course of the i 'th isochrone, W_{0i} limiting volume of adsorption space for the given isochrone, P_0 saturated vapour pressure at temperature T , B constant characterizing the microporosity of adsorbent, W_0 limiting volume of adsorption space (for microporous adsorbents the volume of micropores), a_e equilibrium adsorbed amount expressed in grams per one gram of adsorbent, β affinity coefficient. According to Polanyi⁶, the affinity coefficient equals to the square root of the ratio of the van der Waals constants a of corresponding vapours, according to Dubinin and Timofejev^{7,8}, to the ratio of their molar volumes or to the ratio of their parachors⁹.

Isochrones – both isobaric and isothermal – are not experimentally directly measurable. They can be, however, constructed from single kinetic isotherms which are accessible experimentally. Eq. (5) for isothermal isochrones is more suitable than the equations $P/a - P, X/[a(1 - X)] - X$ which were used for correlation in the paper³ and which for $\tau \rightarrow \infty$ expressed the Langmuir and BET equation and had a limited pressure range. Isothermal isochrones enable us to calculate the kinetic isotherm at another pressure. If Eqs (2) and (3) can be linearized, then we are able to obtain the dependence of the adsorbed amount on pressure and time in the isothermal space diagram from minimum number of experimentally measured kinetic isotherms. As it was shown³, we can express the kinetic isotherm by the equation

$$\tau/a = K_p\tau + M_p, \quad (T, P) \quad (7)$$

where K_p and M_p are constants whose values change with pressure. From the ratio of the intercept and slope of the straight line, the half-time is determined. The depen-

dence of the half-time on pressure for n-pentane and n-hexane at various temperatures was expressed by the relation

$$\tau_{0.5} = kP^{-n}, \quad (8)$$

where n is constant and $\tau_{0.5}$ half-time. By taking the logarithm and differentiating Eq. (8) with respect to temperature at constant adsorbed amount and adsorbent surface we obtain the expression

$$\partial \ln \tau_{0.5} / \partial T = -n(\partial \ln P / \partial T). \quad (9)$$

The dependence of diffusion coefficient on temperature can be expressed as

$$\partial \ln D_e / \partial T = -\partial \ln \tau_{0.5} / \partial T = E / RT^2, \quad (10)$$

for $D_e = kr^2 / (\tau_{0.5}\pi^2)$, where E is activation energy of transfer of the adsorbate, R gas constant, D_e effective diffusion coefficient, k constant characterizing the geometric shape of grain, r radius of the grain, π Ludolf number and T is temperature in K.

Isosteric adsorption heat Q_{iso} is defined² by the equation

$$\partial \ln P / \partial T = Q_{\text{iso}} / RT^2. \quad (11)$$

By combining Eqs (9), (10) and (11), we obtain the relation between the activation energy and the isosteric adsorption heat

$$E = nQ_{\text{iso}}. \quad (12)$$

RESULTS AND DISCUSSION

Maintaining the temperature constant, Eq. (1) can be represented in the isothermal space diagram with the coordinates adsorbed amount, pressure and time. From single kinetic isotherms, which are defined by Eq. (2), we can construct isothermal

TABLE I

Constants of the Dubinin Equation for Adsorbents of the First Structural Type Evaluated from Kinetic Isotherms; Adsorbent Active Carbon "Supersorbon"

Adsorbate	t °C	q g/cm ³	W_0q	W_0 cm ³ /g	k_e^a	$B \cdot 10^6$	
						Ref. 10,	Ref. 7, 8
n-Pentane	20	0.6263	0.2934	0.469	0.030	0.95	1.35
	30	0.6165	0.2893	0.469	0.0319	0.94	1.35
n-Hexane	30	0.6505	0.3047	0.468	0.025	1.06	1.37

$$^a k_e = -0.43 BT^2 / \beta^2.$$

TABLE II
Ratio of Affinity Coefficients of n-Hexane and n-Pentane, Z

Expression	Z	Reference	Expression	Z	Reference
Eq. (6) ^a $\sqrt{(k_{e1}/k_{e2})}$	1.130	Table I	V_2/V_1	1.132	10, 11
β_2/β_1	1.199	13	$\sqrt{(a_2/a_1)}$	1.141	9

^aBy means of slopes for given vapours at the same temperature.

TABLE III
Isothermal Isochrones and Equilibrium Adsorbed Amount of n-Pentane on Active Carbon "Supersorbon"

Temperature 20°C, Eqs (5) and (6) $X = \log^2 (P_0/P)$, $Y = \log a$.

P Torr	X	a, exp (calc) mg/g	δa^a	$-Y \cdot 10^3$, exp (calc)	δY^a
1st minute					
11.83	2.404	140.76 (141.25)	-0.351	851.5 (850.0)	0.179
16.83	1.953	156.82 (155.40)	0.905	804.6 (8.086)	-0.491
26.83	1.428	173.08 (173.64)	-0.325	761.8 (767.3)	0.185
50.97	0.8393	196.18 (196.64)	-0.239	707.4 (706.3)	0.147
77.32	0.5405	207.18 (209.47)	-1.11	683.7 (678.9)	0.700
120.38	0.2947	223.10 (220.64)	1.10	651.5 (656.3)	-0.737
2nd minute					
5.91	3.429	151.08 (151.67)	-0.395	820.8 (819.1)	0.208
11.83	2.404	181.42 (179.39)	1.12	741.3 (746.2)	-0.658
16.83	1.953	194.60 (193.14)	0.752	710.8 (714.1)	-0.461
26.83	1.428	207.93 (210.47)	-1.22	682.1 (676.8)	0.774
50.97	0.8393	229.86 (231.74)	-0.818	638.5 (635.0)	0.554
77.32	0.5405	240.18 (243.36)	-1.32	619.5 (613.8)	0.922
120.38	0.2947	253.50 (253.34)	0.063	596.0 (596.3)	-0.046
167.20	0.1602	263.68 (258.99)	1.78	578.9 (586.7)	-1.35
4th minute					
11.83	2.404	218.86 (217.92)	0.428	659.8 (661.7)	-0.282
16.83	1.953	229.04 (229.23)	-0.084	640.1 (639.7)	0.057
26.83	1.428	241.07 (243.13)	0.855	617.9 (614.2)	0.598
50.97	0.8393	261.29 (259.70)	0.609	582.9 (585.5)	-0.455
77.32	0.5405	267.51 (268.55)	-0.388	572.7 (571.0)	0.294
120.38	0.2947	276.05 (276.05)	0.000	559.0 (559.0)	0.000
167.20	0.1602	281.04 (280.25)	0.283	551.2 (552.5)	-0.223

TABLE III
 (Continued)

P Torr	X	a , exp (calc) mg/g		δa^a	$-Y \cdot 10^3$, exp (calc)		δY^a
5th minute							
11.83	2.404	227.88	(227.42)	0.203	642.3	(643.2)	-0.137
16.83	1.953	237.45	(237.88)	-0.182	624.4	(623.6)	0.127
26.83	1.428	249.27	(250.65)	-0.556	603.3	(600.9)	0.399
50.97	0.8393	268.47	(265.79)	0.999	571.1	(575.5)	-0.763
77.32	0.5405	273.32	(273.82)	-0.183	563.3	(562.5)	0.141
120.38	0.2947	279.81	(280.61)	-0.285	553.1	(551.9)	0.223
167.20	0.1602	284.39	(284.40)	-0.002	546.1	(546.1)	0.000
a_e from kinetic isotherms							
5.91	3.429	231.02	(231.32)	-0.127	636.3	(635.8)	0.087
11.83	2.404	247.90	(248.37)	-0.190	605.7	(604.9)	0.136
16.83	1.953	255.55	(256.27)	-0.280	592.5	(591.3)	0.205
26.83	1.428	266.35	(265.78)	0.216	574.5	(575.5)	-0.163
50.97	0.8393	280.22	(276.85)	1.20	552.5	(557.8)	-0.952
77.32	0.5405	281.86	(282.65)	-0.278	550.0	(548.8)	0.219
120.38	0.2947	286.17	(287.50)	-0.468	543.4	(541.4)	0.373
167.20	0.1602	289.58	(290.20)	-0.213	538.2	(537.3)	0.172

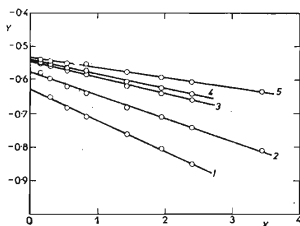
^aDeviation in percent of experimental value.


FIG. 1

Isothermal Isochrones and Equilibrium Adsorption Isotherm of n-Pentane on Active Carbon "Supersorbon" at 20°C

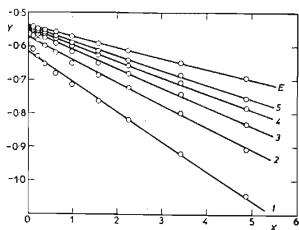
 Minute: 1 1st, 2 2nd, 3 4th, 4 5th, 5 equilibrium. $Y = \log a$ (for isochrone - Eq. (5)), $Y = \log a_e$ (for equilibrium - Eq. (6)), $X = [\log(P_0/P)]^2$.


FIG. 2

Isothermal Isochrones and Equilibrium Adsorption Isotherm of n-Pentane on Active Carbon "Supersorbon" at 30°C

 Numbers at curves denote minutes of measurement, E denotes equilibrium. $Y = \log a$ (for isochrone - Eq. (5)), $Y = \log a_e$ (for equilibrium - Eq. (6)), $X = [\log(P_0/P)]^2$.

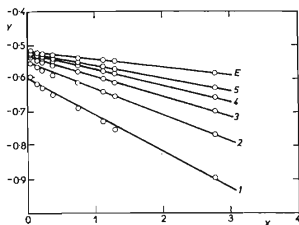
isochrones defined by Eq. (3). Taking into account that Eq. (2) for $\tau \rightarrow \infty$ expresses one point of the equilibrium adsorption isotherm at pressure P and Eq. (3) in infinite time the equilibrium adsorption isotherm, then the agreement of constants W_0 and B in Eq. (6) determined from end points of kinetic isotherms for different adsorbates and temperatures gives an evidence that the data are consistent (Table I). The affinity coefficient in Eqs (5) and (6) may be expressed in different ways. In Table II, the ratios of affinity coefficients of n-pentane as determined from experimental data are compared with data from the literature. The ratio of molar volumes of n-hexane (2) and n-pentane(1) $V_2/V_1 = 1.132$ conforms best to the experimental results and therefore the values of constant B calculated from the ratios of molar volumes of the corresponding adsorbate (n-pentane or n-hexane) related to benzene at the same temperature are presented in Table I. These given values of the constant B show better agreement than those calculated on the basis of the paper¹⁰.

Eq. (3) enables us to use equations for correlating the kinetic isochrones which turn into the equation of the adsorption isotherm in infinite time and therefore their independent variable coordinate is the same as in the equation of isotherm. It was shown³ that for a certain pressure range, equations may be used which in limit express the Langmuir or BET equation. As it was stated^{4,5} the active carbon "Supersorbon" is a fine-porous adsorbent and therefore it is possible to use for the adsorption of vapours in a wide range of pressures the Dubinin equation for adsorbents of the first structural type. In the paper¹, kinetic data were correlated for the temperature range near the critical temperature and in this work, an attention is paid to the temperatures which satisfy the condition $T \leq 0.8T_k$. In Table III are given kinetic data for n-pentane at the temperature of 20°C (Fig. 1) for single isochrones expressed by Eq. (5) and the equilibrium data obtained from end points of kinetic isotherms. The results show the suitability of the equation used (Eq. (5)), for unlike the work³, the wide range of pressures for the given isochrone is to be expressed by one equation. Experimentally determined values of the adsorbed amount and the values calculated according to Eqs (5) and (6) show a satisfactory agreement. For measuring the kine-

FIG. 3

Isothermal Isochrone and Equilibrium Adsorption Isotherm of n-Hexane on Active Carbon "Supersorbon" at 30°C

Numbers at curves denote minutes of measurement, E denotes equilibrium. $Y = \log a$ (for isochrone — Eq. (5)), $Y = \log a_e$ (for equilibrium — Eq. (6)), $X = [\log(P_0/P)]^2$.



tics, deviations of the adsorbed amount are within the range which is acceptable even for the equilibrium adsorption isotherm. This method of correlation is more suitable for the wide pressure range than the use of the Langmuir or BET equation (Figs 2, 3).

In Eq. (9) the activation energy of transfer of the adsorbate is compared with the isosteric heat. The constants of Eq. (8) are: for n-hexane $n = 0.53 \pm 0.02$, $k = 2.14 \pm 0.02$ at the temperatures 0, 30, and 50°C, for n-pentane $n = 0.45 \pm 0.02$, $k = 2.14 \pm 0.03$ at the temperatures 0, 10, 20, 30, 40, 50 and 120°C.

If the value of the constant $n = 0.5$, then it follows from Eq. (12) that the activation energy of transfer of the adsorbate is equal to a half of the isosteric heat. Thus, according to the papers^{11,12}, the surface diffusion may take place both for n-pentane and n-hexane. If a concentration gradient exists in the adsorbed phase¹³, then the activation energy of transfer of the adsorbate is to be equal to the adsorption heat reduced by the contribution due to the presence of micropores and its value depends on their dimensions.

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