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Recent Equilibrium and Kinetic Studies of the Adsorption of Gases and Vapours by Microporous Adsorbents

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Thermodynamic theories of adsorption equilibrium in micropores are discussed with special reference to the osmotic theory of adsorption, based on the vacancy solution model, and to the analogy between adsorption and osmotic equilibria. A thermal adsorption equation is derived, and its special cases are discussed, thus giving a quantitative description of adsorption on microporous adsorbents over a wide range of pressure and temperature. New methods of investigating the kinetics of vapour adsorption on microporous adsorbents and of describing the process theoretically by the bipore model are reviewed. Good agreement between experiment and theory is obtained. 40 references.

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I. INTRODUCTION

This review describes the most important results obtained in recent years in the Sorption Processes Section of the Institute of Physical Chemistry of the USSR Academy of Sciences. We shall discuss the theoretical and experimental studies of equilibrium physisorption carried out by Bering and Serpinskii with the cooperation of Yakubov and Fomkin, and the studies of the kinetics of physisorption on adsorbents with a bipore structure by Zolotarev and Voloshchuk with Erashko, Gorlov, Shen, and Ulin.

II. ADSORPTION EQUILIBRIA ON MICROPOROUS ADSORBENTS

Zeolites are typical microporous adsorbents. The similarity in size between the micropores and the adsorbed molecules produces a marked increase in the adsorption potential associated with dispersion forces. The presence of cations in the zeolite holes causes a large increase (by electrostatic interactions) in the energy non-uniformity of the adsorption sites of the micropores as compared with similar but chemically different adsorbents (e.g. carbons).

Our experimental and theoretical studies of the equilibrium adsorption of various vapours on micropores, started in 1946, have gradually led to the concept of a qualitative difference between adsorption in micropores and adsorption on non-porous or coarsely porous surfaces of a similar chemical nature. The theory of volume filling of micropores was proposed as a reasonable approximation to the description of adsorption in micropores [1-4]. We shall outline below only those aspects of this theory which are needed for the later discussion.

The most important function used in this theory is the differential molar heat of adsorption A,

$$A = -\Delta G = RT \ln (p_s/p), \quad (1)$$

which expresses the negative change in the Gibbs free energy G when the standard state is defined as the normal liquid at temperature T in equilibrium with its saturated vapour. In general the equilibrium vapour pressure and the saturation vapour pressure are replaced by the corresponding fugacities in order to correct for the non-ideality of the vapour.

The limiting adsorption a_0 corresponds to filling of the micropore volume, which can be treated as constant to a good approximation. Hence the temperature dependence of a_0 can be expressed as

$$a_0 = a_0^0 \exp [-\alpha (T - T_0)], \quad (2)$$

where α is the volume expansion coefficient of the adsorbate, which can be calculated approximately from the physical properties of the substance to be adsorbed (adsorband) [4]. If the adsorption at the equilibrium pressure p and temperature T is a, the coverage θ is defined as a/a_0.

The fundamental theoretical postulate of temperature invariance

$$(\partial A/\partial T)_\theta = 0 \quad (3)$$

was taken as an experimental fact from the work of Polanyi [5,6]. However the interpretation of the function A [Eqn. (1)] as an adsorption potential and the attempt to justify the postulate (3) in terms of adsorption layers in micropores with equipotential surfaces are not entirely convincing. It should be noted that the experimental evidence for Eqn. (3) was obtained [4] not with relatively coarsely porous (e.g. mesoporous) adsorbents as expected but with typically microporous adsorbents such as active carbons.

By treating the temperature-independent characteristic adsorption equation $\theta = f(A)$ as a distribution of coverages with respect to differential molar free energy of adsorption, expressed in the form of the statistical Weibull equation, we arrive at the thermal adsorption equation

$$a = a_0 \exp\left[-(A/E)^n\right], \quad (4)$$

where E is the characteristic adsorption energy ($E = A$ for $\theta = 1/e$) and n is a small integer having a value between 2 and 6 in the main variant of the theory [2]. The temperature independent parameters of the distribution function of E and n are also parameters of Eqn.(4). This equation, combined with Eqns.(1) and (2), gives the thermal adsorption equation

$$a = a_0 \varphi(p/p_s, T). \quad (5)$$

We have shown [3,4] that both the adsorption equilibria and the corresponding differential heats of adsorption $Q(\theta)$ are satisfactorily described by Eqn.(4) in many adsorption systems involving microporous adsorbents, and in particular in zeolites. However the assumed temperature invariance of A is only a rational approximation, which can be applied with acceptable precision only in the most favourable cases and in the temperature range 100° to 150°C. Furthermore it can predict only a decrease in differential heat of adsorption with increasing coverage. Heats of adsorption increasing with coverage lie outside the scope of the theory.

These considerations point to the need for a more perfect model of the equilibrium adsorption of vapours in micropores and for theoretical and computational approaches free from the above shortcomings. Bering and Serpinskii have developed and experimentally validated a more general theory of the thermodynamics of adsorption equilibria which has been termed the osmotic theory of adsorption [7]. We shall discuss the main variant of the theory with reference to microporous adsorbents.

III. FUNDAMENTALS OF THE OSMOTIC THEORY OF ADSORPTION IN MICROPORES

Hill has shown [8] that physisorption equilibria between an adsorbent and a gas phase can be described either by adsorption thermodynamics or by solution thermodynamics. The adsorbent is usually assumed to be thermodynamically inert towards adsorption, and the methods of adsorption thermodynamics are used. However in microporous adsorbents like zeolites the linear dimensions of the crystallites vary during adsorption [9]. In this case the chemical potential of the adsorbent also varies, and it becomes more convenient to use the methods of solution thermodynamics.

This approach to the description of adsorption equilibria is particularly successful when used in conjunction with the solution model which has been termed the "vacancy solution". In this model the so-called adsorption vacancies are treated as one of the components of the solution in place of the solid adsorbent [10]. The term adsorption vacancy denotes the free elementary volume of the adsorption space of the micropores which is filled by one molecule of adsorbate during adsorption. Since the adsorption space of the micropores is limited by the micropore volume, we can define a maximum number of vacancies (equal to the limiting number of adsorbed molecules) per unit mass of the adsorbent. The adsorption tends asymptotically towards this number as the pressure of adsorband in the gas phase rises towards infinity. At any finite equilibrium pressure of the adsorband the adsorption space of the micropores contains adsorbed molecules and adsorption vacancies, which constitute the binary vacancy solution. At constant temperature the relationship between the equilibrium pressure in the gas phase and the mole fraction of solute (adsorbate), i.e. the extent of adsorption, is equivalent to a partial pressure curve for the vacancy solution or to an adsorption isotherm. Thus adsorption equilibrium between the adsorbent and the gas phase is equivalent to equilibrium between the vacancy solution and the same gas phase. In this model all the properties of the adsorbent are treated as properties of the vacancies, i.e. of the solvent. An adsorption equilibrium of this type is most conveniently analysed by solution thermodynamics.

These ideas have proved to be very fruitful because a physical as well as a formal thermodynamic analogy exists between adsorption equilibrium and osmotic equilibrium. This analogy was first recognised, for the simplest case of adsorption at a liquid surface, by Frumkin [11] in 1925, and it was subsequently formulated in detail by Adam [12]. Unfortunately it was not developed further.

Let us consider the physical basis of this analogy. We shall denote the number of moles of adsorbate and the number of vacancies per unit mass of the adsorbent by a and a^* respectively. For any equilibrium situation we have

$$a + a^* = a_m, \quad (6)$$

where a_m is the limiting adsorption, assumed to be independent of temperature. We now define the mole fractions of adsorbate (x) and of vacancies (x^*) in the vacancy solution as

$$x = a/a_m, \quad x^* = a^*/a_m. \quad (7)$$

We shall treat the equilibrium between a microporous adsorbent and a gas phase as an equilibrium between two vacancy solutions at different concentration. One of these is the vacancy solution in the micropores, the other is a solution of adsorband molecules in a vacuum. In the latter solution the role of "solvent" is played by vacancies in the gas phase. Two solutions of the same components at different concentration can be in equilibrium only if one of them is exposed to an external potential field. It can easily be shown that the effect of this field is formally equivalent to a difference in hydrostatic pressure between the solutions. This difference is termed the osmotic pressure in solution theory.

We shall write expressions for the chemical potentials of the vacancies in these two solutions, using the subscript α to denote the quantities relating to the gas phase. The vacancy solution corresponding to the gas phase is always very dilute, and can be treated as an ideal solution:

$$\mu_\alpha^* = \mu_{\alpha 0}^* + RT \ln x_\alpha^* + p_\alpha V^*, \quad (8)$$

$$\mu^* = \mu_0^* + gRT \ln x^* + pV^*, \quad (9)$$

where V^* is the molecular volume of the vacancies and g is the osmotic coefficient which characterises (like an activity coefficient) the non-ideality of the vacancy solution in the micropores [13].

At equilibrium $\mu_\alpha^* = \mu^*$, and from Eqns.(8) and (9) we have

$$\mu_{\alpha 0}^* + RT \ln x_\alpha^* + p_\alpha V^* = \mu_0^* + gRT \ln x^* + pV^*. \quad (10)$$

When $x_\alpha^* = 1$, i.e. at zero concentration of the adsorband in the gas phase, we can write $x^* = 1$, $g = 1$, and $p_\alpha = p$.

Hence $\mu^*_{\alpha 0} = \mu^*_0$ in Eqn.(10). Defining the osmotic pressure as

$$\Pi = p - p_a, \tag{11}$$

we obtain

$$\Pi V^* = -gRT \ln x^* + RT \ln x^*_a. \tag{12}$$

As was pointed out above, the vacancy solution in the gas phase is very dilute, and $x^*_\alpha \simeq 1$: therefore the second term in Eqn.(12) can be ignored. If W is the volume of micropores per unit mass of adsorbent the ratio W/V^* is the limiting adsorption a_m:

$$W/V^* = a_m. \tag{13}$$

From Eqns.(12), (13), and (7) we obtain

$$W\Pi = -a_m gRT \ln (1 - a/a_m). \tag{14}$$

We now write the Gibbs–Duhem equation for the vacancy solution in the micropores, taking unit mass of the adsorbent at T = const:

$$a\,d\mu + a^*\,d\mu^* = W\,d\Pi, \tag{15}$$

where μ is the chemical potential of the adsorbate. Since this solution is in osmotic equilibrium $d\mu^* = 0$, and therefore

$$a\,d\mu = W\,d\Pi. \tag{16}$$

Hence $\Pi = (1/W)\int_0^a a\,d\mu = \Phi/W$, where Φ is the integral of the Gibbs adsorption equation calculated from the adsorption isotherm. Obviously the value of Φ is proportional to the osmotic pressure of the vacancy solution in the micropores.

Introducing the only non-thermodynamic assumption of our argument—constancy of the osmotic coefficient g at T = const—we obtain the adsorption isotherm equation from Eqns.(14) and (16). Eqn.(14) is differentiated to give $d\Pi$ which is inserted into (16), from which we obtain an expression for $d\mu$:

$$d\mu = \frac{a_m gRT}{a(a_m - a)}\,da. \tag{17}$$

Integration of Eqn.(17) gives

$$\mu = \mu^0 + RT \ln p = gRT \ln \frac{a}{a_m - a} + K, \tag{18}$$

leading to the adsorption isotherm

$$p^{1/g} = \frac{a/\beta}{a_m - a}, \tag{19}$$

where K is an integration constant and β is a constant, or

$$a = a_m \beta p^{1/g}/(1 + \beta p^{1/g}). \tag{20}$$

Eqn.(20) has been used for a long time as an empirical adsorption isotherm with three parameters a_m, β, and g (see, for example, Ref.14). The successful use of this equation over a wide range of coverages a/a_m confirms the validity of our assumption of a constant osmotic coefficient g at constant temperature.

The only temperature-dependent parameters of the adsorption isotherm equation (20) are g and β. Expressions for their temperature dependence can be obtained from two almost self-evident non-thermodynamic assumptions. By analogy with the osmotic equilibrium we assume that the osmotic coefficient g is a linear function of reciprocal temperature[15]:

$$g = C\left(1 - \frac{b}{T}\right), \tag{21}$$

and we further assume that this expression is a good approximation over a wide range of coverage. To express the temperature dependence of the parameter β we assume that the adsorption isostere is linear at half-coverage (i.e. for $a = 0.5a_0$):

$$\ln p_{0.5} = C_{0.5} - \frac{L_{0.5}}{T}. \tag{22}$$

Introducing the symbol

$$\varphi(a) = \ln \frac{a}{a_m - a}, \tag{23}$$

and taking logarithms of Eqn.(19) we find

$$\ln p = g\varphi(a) - g \ln \beta. \tag{24}$$

Since $\varphi(a) = 0$ at $a = 0.5a_m$ we can write in this case

$$\ln p_{0.5} = -g \ln \beta. \tag{25}$$

Equation (26) for the temperature dependence is obtained in the form $f(a,p,T) = 0$ of the osmotic theory of adsorption by inserting g from (21) and $\ln p_{0.5}$ from (25) into Eqn.(24), with allowance for Eqn.(22):

$$\ln p = C_{0.5} - L_{0.5}/T + C(1 - b/T) \ln \frac{a}{a_m - a}. \tag{26}$$

This equation can be written

$$\ln p = C_a - L/T, \tag{27}$$

where

$$C_a = C_{0.5} + C\varphi(a) \tag{28}$$

and

$$L = L_{0.5} + Cb\varphi(a) \tag{29}$$

are temperature-independent parameters. However their relationship to the amount of adsorption can be shown explicitly by using Eqn.(23).

Thus the thermal adsorption equation (26) has been obtained from the known adsorption isotherm (19), the thermodynamic variation of the osmotic coefficient with temperature (21), and the empirically justified assumption (22). The equation corresponds to linear isosteres over a wide range of adsorption values: linearity of the adsorption isosteres is known to be a universal property of adsorption equilibria, and is usually observed experimentally.

We note that in the initial portion of the adsorption isotherm, when the adsorption is very small and the vacancy solution approaches ideal behaviour at infinite dilution, the osmotic coefficient g tends towards unity and the parameter b tends towards zero. Thus it can be assumed that $g = 1$ in the initial portion of any adsorption isotherm, but as a increases this coefficient rapidly changes to some other value which remains constant over a wide range of adsorptions.

IV. EXPERIMENTAL FOUNDATIONS OF THE THERMAL EQUATION OF THE OSMOTIC THEORY OF ADSORPTION

The thermal adsorption equation (26) contains five parameters: a_m, $L_{0.5}$, $C_{0.5}$, C, and b, and in order to determine their values we need at least two experimental adsorption isotherms for temperatures T_1 and T_2, which must not be too close. The parameter a_m can be evaluated from one of the isotherms (see below), and corresponding values of $\ln p_1$ and $\ln p_2$ are then found from the isotherms, by interpolation, for two or three suitable

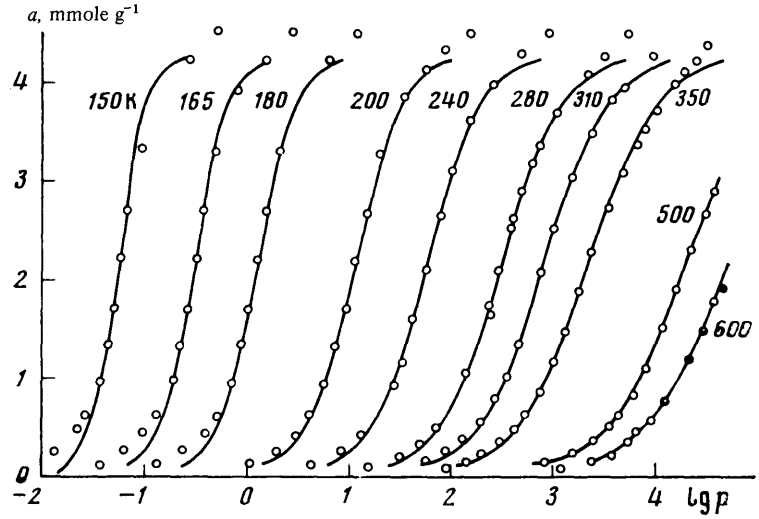


Figure 1. Adsorption isotherms of Xe on NaX zeolite. Full lines are calculated by Eqn. (26), circles are experimental.

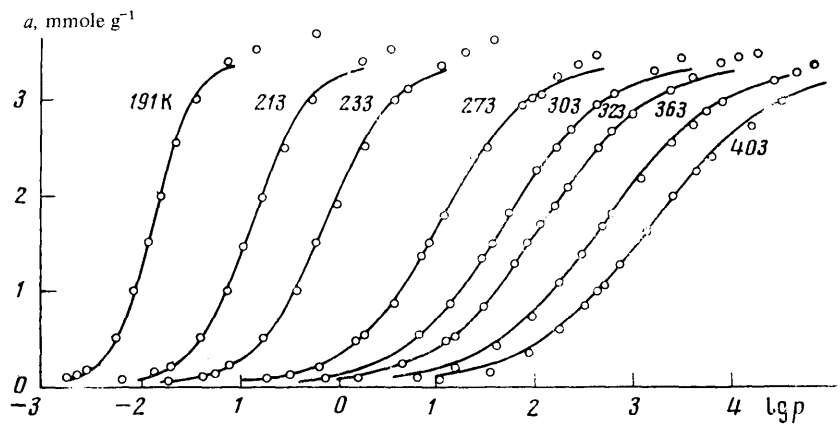


Figure 2. Adsorption isotherms of CF_3Cl on NaX zeolite. Full lines are calculated by Eqn. (26), circles are experimental.

values of the adsorption. The parameters C_a and L are calculated by Eqn. (27) for the chosen values of a = const, and $C_{0.5}$ and C are determined by Eqn. (28). $L_{0.5}$ and b are determined similarly by Eqn. (29).

The thermal equation (26) of the osmotic theory of adsorption gives a very accurate description of adsorption equilibria of gases and vapours on different microporous adsorbents such as zeolites and active carbons over a wide range of temperature and pressure. We shall illustrate the agreement between theory and experiment by considering two of the systems which have been studied in the writer's laboratory[16,17]: Xe on NaX zeolite and CF_3Cl on NaX zeolite. This work is experimentally interesting because the apparatus developed for it has proved suitable for precise measurements of adsorption equilibria over very wide ranges of pressure (from $\sim 10^{-2}$ mmHg to 100 atm) and of temperature (from 150 to 600 K).

Plots of a against lg$p$ in Fig. 1 show as full lines the adsorption isotherms of Xe on crystals of NaX zeolite calculated for different temperatures by Eqn. (2) with the following values of the parameters: a_m = 4.30 mmole g^{-1}, $L_{0.5}$ = 1225 K, $C_{0.5}$ = 6.76, C = 1.14, and b = 109 K. The agreement between theory and experiment is good in the range of coverage (a/a_m) from 0.09 to 0.93 for a wide range of temperature (150–600 K) including the critical temperature of the adsorband (T_c = 290 K). An analogous family of isotherms for the adsorption of CF_3Cl on the same sample of NaX zeolite is shown in Fig. 2. The parameters a_m = 3.40 mmole g^{-1}, $L_{0.5}$ = 1850 K, $C_{0.5}$ = 7.80, C = 2.38, and b = 154 K were used for calculations by Eqn. (26). The experimental temperature range again

includes the critical temperature (T_c = 302 K), and the agreement between theory and experiment is again good for coverages between 0.09 and 0.97.

It is important to note that the adsorption isosteres are linear in both systems for this range of coverage. The thermal adsorption equation (26) applies at temperatures both above and below the critical temperature with the same set of parameters. The excellent agreement between the calculated and the experimental adsorption isotherms and the linearity of the isosteres (e.g. for $a = 0.5a_m$) are direct experimental confirmation of the validity of the basic assumptions of the osmotic theory of adsorption: constancy of the osmotic coefficient g at T = const and linearity of the standard adsorption isostere.

V. THERMODYNAMIC ADSORPTION EQUILIBRIUM FUNCTIONS

Expressions for the main thermodynamic functions of the adsorption equilibrium in the range of p and T values for which the gas phase can be treated as almost ideal are easily obtained from Eqns. (22) and (29). According to Eqns. (24) and (25) the differential Gibbs free energy G is given by the expression

$$G = RT \ln p = G_{0,s} + gRT\varphi(a). \tag{30}$$

Differentiating this expression with respect to T with a = const, and allowing for the temperature dependence of g [Eqn. (21)], gives an expression for the differential entropy of adsorption S:

$$S = -(\partial G/\partial T)_a = S_{0,s} - CR\varphi(a). \tag{31}$$

If the equilibrium gas phase is ideal we have $RL = Q$, where Q is the differential heat of adsorption. Hence, from Eqn. (29),

$$Q = Q_{0,s} + CbR\varphi(a). \tag{32}$$

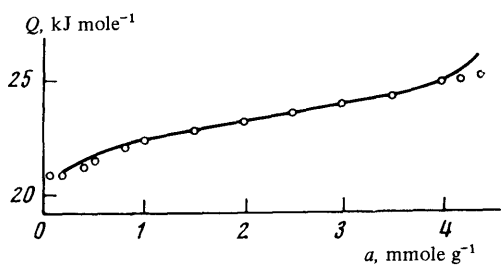


Figure 3. Differential heat of adsorption of Xe on NaX zeolite against a. The full line is calculated by Eqn. (32), the circles are experimental values of Q.

It can be shown by thermodynamic arguments that the parameter C in formula (21) cannot be negative. Hence it follows from Eqn. (32) that for T = const the dependence of the heat of adsorption Q on a is determined by the sign of the parameter b. For $b > 0$, Q increases with adsorption (and coverage), whereas for $b < 0$ Q decreases as a increases.

The variation with adsorption of the differential heat calculated by Eqn. (32) (full line) is compared in Fig. 3 with experimental results for the Xe–NaX system at T = 165 K in the region of p values for which the gas phase can be treated as ideal. The agreement between calculation and experiment is satisfactory.

Thus the osmotic theory of adsorption equilibria leads to a thermal adsorption equation which allows us to express the isotherms, isosteres, and thermodynamic equilibrium functions in terms of a single set of parameters.

VI. COMPARISON OF CALCULATIONS USING VARIOUS EQUATIONS OF ADSORPTION IN MICROPORES

A computer study has shown [18] that the parameters of the adsorption equations given by the micropore volume filling theory and the osmotic theory of adsorption can be optimised to enable Eqns. (4) and (20) to describe accurately the same experimental results over a wide range of coverage:

$$a_m = \varkappa a_0 \tag{33}$$

$$g = \frac{E}{RT}F \tag{34}$$

$$\ln\beta = \left[\frac{\ln(2/\varkappa)}{F}\right]^{1/n} - \frac{1}{g}\ln p_s. \tag{35}$$

Table 1. Conversion coefficients.

n	$\varkappa$	F		θ_{min}	θ_{max}
2	1.182	0.3440	2.109	0.21	0.91
3	1.054	0.2228	3.869	0.35	0.96
4	1.025	0.1696	5.330	0.46	0.98

Table 2. Adsorption isotherms of methane on zeolite L.

T=156 K *			T=156 K *			T=243 K **			T=243 K **		
p, mmHg	a, mmole g⁻¹*** TVF	OTA	p, mmHg	a, mmole g⁻¹*** TVF	OTA	p, mmHg	a, mmole g⁻¹*** TVF	OTA	p, mmHg	a, mmole g⁻¹*** TVF	OTA
3	0.709	0.714	100	1.814	1.813	500	2.099	2.098	1 500	1.236	1.239
5	0.871	0.872	120	1.857	1.855	400	0.635	0.640	2 000	1.361	1.364
10	1.105	1.104	140	1.891	1.888	450	0.685	0.689	3 000	1.519	1.521
20	1.339	1.341	160	1.919	1.916	500	0.731	0.734	4 000	1.617	1.617
40	1.562	1.564	200	1.963	1.958	750	0.916	0.917	6 000	1.731	1.728
60	1.681	1.682	250	2.002	1.998	1000	1.050	1.052	10 000	1.835	1.833
80	1.758	1.758									

*Assuming a_0 = 2.207 mmole g^{-1}, n = 3, E = 2.350 kcal mole^{-1}, a_m = 2.213 mmole g^{-1}, g = 1.539, β = 0.2281, f_s = 8200 mmHg.

**Assuming a_0 = 1.934 mmole g^{-1}, n = 3, E = 2.350 kcal mole^{-1}, a_m = 2.213 mmole g^{-1}, g = 1.237, β = 0.003315, f_s = 62 000 mmHg.

***TVF denotes calculation by the equation of the theory of volume filling, OTA denotes calculation by the equation of the osmotic theory of adsorption.

The conversion coefficients κ, F, and y for the adsorption systems to which Eqn. (4) is applicable are listed in Table 1, together with the ranges of coverage $\theta = a/a_m$ within which formulae (33)–(35) can be used with adequate

precision at temperatures between 100 and 150 K. As an example, points on the isotherm for the adsorption of methane on zeolite L calculated by Eqns. (4) and (20) for 156 K are compared in Table 2. The range of coverages θ lies within the limits given in Table 1 for $n = 3$. The results of the calculations are almost indistinguishable. However the osmotic theory of adsorption allows us to describe adsorption equilibria in microporous adsorbents over wider ranges of pressure and temperature, and in particular above the critical point.

VII. THE BIPORE MODEL OF MICROPOROUS ADSORBENTS IN THE KINETICS OF PHYSICAL ADSORPTION

Pores in adsorbents can be classified [4,19] according to the mechanism of the adsorption and of the capillary phenomena in the adsorbent grains into micropores ($r < 6-7$ Å), supermicropores ($6-7 < r < 15-16$ Å), mesopores ($15-16 < r < 1000-2000$ Å), and macropores ($r > 1000-2000$ Å). The symbol r denotes the equivalent pore radius, equal to twice the ratio of the normal cross-sectional area to the perimeter of the pore.

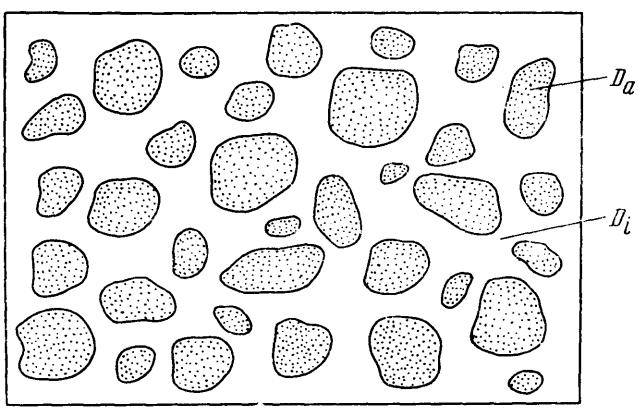


Figure 4. Model of the biporous adsorbent.

In many practical cases we can simplify the structure of the adsorbent and consider only two types of pore with very different properties: adsorption pores (micro- and supermicropores) and transport pores (meso- and macropores). This bipore model of the adsorbent, which can be applied successfully to zeolites, is illustrated in Fig. 4. The grey areas represent microporous regions of the adsorbent, consisting exclusively of adsorption pores. The transport pores are located in the region between the microporous regions.

The adsorption kinetics of biporous adsorbents have been studied by other workers [20-24] as well as in our laboratories [25-39]. The equations of inner diffusion in biporous adsorbents have been investigated for the general case of non-linear adsorption isotherms, and generalised for microporous regions (crystals) of difference size with a finite diffusional resistance to the entry of molecules into the crystal [26,28,31,32]. The latter resistance arises from the potential barrier at the boundary of the microporous region which the molecules must overcome. By using the statistical moment method fairly simple analytic expression can be obtained relating the characteristic times of diffusion in adsorption pores (τ_a) and in transport pores (τ_i) to the moments of the kinetic curves [28-33]. For inner-diffusion kinetics in microporous regions of equal size the first- and second-order moments are

$$M_1 = g_{\nu 1}\tau_i + g_{\mu 1}\tau_a,$$
$$M_2 = g_{\nu 2}\tau_i^2 + 4g_{\nu 1}g_{\mu 1}B\tau_i\tau_a + g_{\mu 2}B\tau_a^2. \qquad (36)$$

In these equations $\tau_i = L^2(1+\Gamma)/D_i$, $\tau_a = r_0^2/D_a$, $\Gamma = a_0/c_0$, L and r_0 define the size of the granule and of the microporous regions, D_i and D_a are the diffusion coefficients for the transport pores and for the microporous regions respectively, a_0 is the equilibrium value of the adsorption, c_0 is the concentration of adsorband at the surface of the granule. For industrial adsorbents we can take $B = 1$. The coefficients $g_{\nu 1}$, $g_{\mu 1}$, $g_{\nu 2}$, $g_{\mu 2}$ are determined by the geometric shape of the granule and of the microporous regions: their values for various assumed geometries are tabulated, for example, in Ref. 33. We have discussed and generalised Eqns. (36) by allowing for a distribution of crystal sizes and for the finite diffusional resistance to the entry of adsorbate molecules into zeolite crystals [31,32]. We have also developed a method of determining the coefficients in biporous adsorbents by monitoring the diffusion of the adsorband between two vessels through a granule of the adsorbent [34]. The diffusion coefficients for the adsorption pores and the transport pores have been determined separately by using the above expressions, and the transport mechanism in real microporous adsorbents such as zeolites and active carbons has been analysed [33,34]. The analysis has confirmed the validity of the bipore model of real microporous adsorbents.

A comparison [35] of calculated and experimental results has shown that the equations of the bipore model can be used to describe the sorption kinetics of low-molecular compounds (benzene, hexane) on two-phase polymer systems such as block copolymers and mixed polymers for the case of a linear adsorption isotherm. Furthermore these polymer systems can be treated as real models of a biporous medium, since their diffusional, structural, and sorption characteristics can be quantitatively determined by independent methods.

Considerable interest has been shown in the direct calculation of $\gamma(t)$ kinetic curves (where γ is the relative adsorption averaged over a grain) for a biporous adsorbent with different ratios of the τ_i and τ_a relaxation times. Computer calculations for linear adsorption isotherms and spherical, cylindrical, or flat adsorbent grains have been reported [36,37].

VIII. KINETICS OF PHYSISORPTION ON BIPOROUS ADSORBENTS FOR SHARPLY CONVEX ADSORPTION ISOTHERMS

The inner diffusion equations for biporous adsorbents have been studied in our laboratory for the case of linear adsorption isotherms [25,26,28-33] and also for sharply convex isotherms quickly approaching saturation ("rectangular" isotherms) [39,40]. We examined the case of cylindrical (or prismatic) adsorbent grains with an impermeable side surface, and we studied changes in the local concentration of adsorbate in the grain as a function of time [$a(x)$, where

x is the distance from the end-face of the grain] as well as changes in the relative adsorption averaged over the grain [$\gamma(t)$, the kinetic curve]. The result is strongly dependent on the ratio of the characteristic times for the establishment of adsorption equilibrium in the transport pores and in the microporous regions (τ_i and τ_a respectively).

With sharply convex isotherms we can obtain a clear picture, which confirms the validity of the bipore model of zeolites and microporous active carbons, by studying the adsorption kinetics of vapours which give X-ray contrast under irradiation with X-rays [25,27,33]. The main advantage of this method is the possibility of visual observation of the formation and propagation of an adsorption front in the adsorbent grain. Consider a cylindrical grain of zeolite in which the side surface and one of the end faces are impermeable, and adsorption of an X-ray contrasting vapour is proceeding from the other end-face (Fig. 5). If the rate of adsorption is determined by diffusion in the zeolite crystals ($\tau_a \gg \tau_i$) the X-ray pictures show a gradual darkening of the entire adsorbent granule (Fig. 5*a*). On the other hand if the process is limited by diffusion in the transport pores ($\tau_i \gg \tau_a$) we expect a sharp adsorption front to be created in the case of a sharply convex adsorption isotherm, i.e. the zeolite granule should be filled "layer by layer" (Fig. 5*c*). In this case the adsorption wave $a(x)$ is almost rectangular in shape, and the kinetic curve is $\gamma(t) \propto \sqrt{t}$.

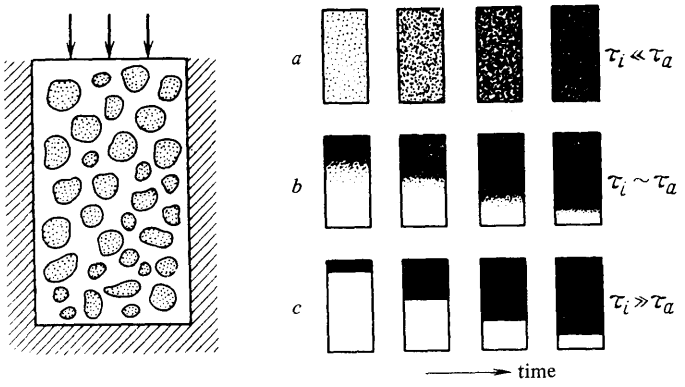


Figure 5. Granule of formed zeolite with an impermeable side surface (adsorption flow is indicated by arrows) and distribution of adsorbate in the adsorbent granule for different relative values of τ_a and τ_i.

In the intermediate case (when τ_i and τ_a are comparable) we observe the formation and propagation through the grain of an adsorption wave [$a(x)$] with a diffuse front (Fig. 5*b*). In this case theory predicts [38,39] a $\gamma(t)$ variation more complex than a simple $\sqrt{t}$ law. The exact form of the $\gamma(t)$ relationship is determined by the form of the kinetic function describing the filling of the microporous regions such as the zeolitic crystallites within the grain [$\varphi(t)$, where $0 \leq \varphi(t) \leq 1$]. We have obtained, for this case, an approximate integral equation for the law of motion of the leading front of the adsorption wave $l(t)$ (Fig. 6):

$$\hat{l}^2(s) = \frac{2D_i}{s^2[(a_0/c_0)\, s\hat{\varphi}(s) + 1/6]}, \qquad (37)$$

where

$$\hat{l}^2(s) = \int_0^\infty e^{-st} l^2(t)\, dt \text{ and } \hat{\varphi}(s) = \int_0^\infty e^{-st}\varphi(t)\, dt \qquad (38)$$

are the transforms of the functions $l^2(t)$ and $\varphi(t)$. In particular, an analytic solution was obtained for the kinetic functions $\varphi(t) = 1 - \exp(-t/\tau_a)$ and $\varphi(t) = 6\sqrt{t/\pi\tau_a}$, where $\tau_a = r_0^2/D_a$ is the characteristic time for diffusion in the micropores, which provide a model of the diffusional mechanisms operating in the initial and the final stages of adsorption in the microporous regions. If the function $\varphi(t)$ is more complex, $l(t)$ can be obtained from Eqn. (37) by numerical inversion of the Laplace transform. The deviation from the true solution introduced by the use of Eqn. (37) is less than 5% in the limiting case ($\tau_a = 0$). In principle Eqn. (37) allows us to determine the kinetics of adsorption in the microporous regions [$\varphi(t)$] from the known equation of motion of the leading front of the adsorption wave [$l(t)$], and vice versa. The equation can also be used to calculate the diffusion coefficients.

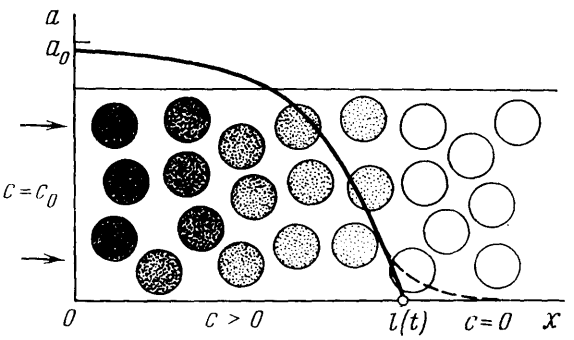


Figure 6. Adsorption front in a granule of biporous adsorbent. The filling of the crystals is indicated qualitatively by the darkening of the circles.

We have also studied theoretically the time dependence of the width of the front of the adsorption wave in the intermediate case ($\tau_i = \tau_a$). [39] For a rectangular adsorption isotherm we found that this quantity (Δt) decreases with time. The exact form of the falling function $\Delta(t)$ depends on the form of the kinetic function which describes the filling of the micropores [$\varphi(t)$]. In particular, if $\varphi(t) = 1 - \exp(-t/\tau_a)$, we have

$$\Delta(t) = \sqrt{\frac{2D_i\tau_a c_0}{a_0}}\left[\sqrt{\frac{t}{\tau_a} + \ln(1-\varepsilon_1) + 1} - \sqrt{\frac{t}{\tau_a} + \ln\varepsilon_1 + 1}\right]. \qquad (39)$$

In this expression $\epsilon_1 > 0$ is a small quantity used in the definition of the width of the adsorption wave front $a(x)$:

$$\Delta(t) = x_2(t) - x_1(t)$$
$$a(x_1)/a_0 = 1 - \varepsilon_1, \quad a(x_2)/a_0 = \varepsilon_1. \qquad (40)$$

The theoretical prediction of a changing width of the adsorption wave front can be tested experimentally by studying the adsorption kinetics of substances opaque to X-rays. We have used this method to study the adsorption kinetics of ethyl iodide, ethyl bromide, and bromobenzene from a stream of nitrogen on CaA, CaX, and NaX zeolites, and on active carbons. Adsorption on the type-X zeolites and on active carbons from a stream of carrier

gas gave a clear indication of "layer by layer" filling of the granules (Fig. 5*c*). With CaA zeolites containing different binders and with granules formed in different ways all three cases were observed (Fig. 5). The intermediate situation ($\tau_i \simeq \tau_a$, Fig. 5*b*) is most easily observed in the adsorption of bromobenzene and xenon from a one-component gas phase on microporous active carbons with molecular-sieve properties [33,40]. The results of these experiments are shown in Fig. 7. Initially the adsorption front is quite diffuse in all the series of photographs, but it becomes sharper with time and at long enough times we observe "layer by layer" filling of the granules.

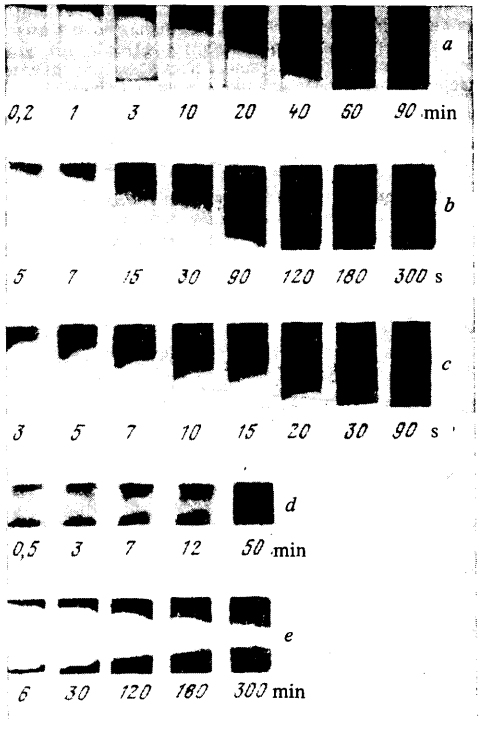


Figure 7. Distribution of xenon (*a*, *b*, *c*) and bromobenzene (*d*, *e*) in a granule of active carbon at successive times. The temperature is T = 195 K (*a*, *b*, *c*) or T = 303 K (*d*, *e*); pressure of adsorband p = 0.9 kPa (*a*), 13.3 kPa (*b*), 26.6 kPa (*c*), 27 Pa (*d*), concentration of adsorband c = 10 mg litre^{-1} (*e*).

IX. THE STATISTICAL MOMENT METHOD AND ANALYSIS OF EXPERIMENTAL DATA ON ADSORPTION KINETICS

The statistical moment method has been widely used in recent years for analysing quantitatively experimental data on the kinetics of adsorption on biporous adsorbents with linear adsorption isotherms. It can be shown that in the case of rectangular adsorption isotherms the statistical moments of the kinetic curve M_k can also be related to the law of motion of the boundary $t_*(x)$ and to the moments of the kinetic filling function of the microporous regions $M_{\varphi k}$ by analogous expressions, which in this case take the form

$$M_1 = M_{\varphi_1} + \frac{1}{R}\int_0^R t_*(x)\,dx, \qquad (41)$$

$$M_2 = M_{\varphi_2} + 2M_{\varphi_1}\frac{1}{R}\int_0^R t_*(x)\,dx + \frac{1}{R}\int_0^R t_*^2(x)\,dx \qquad (42)$$

where R is the characteristic dimension of the adsorbent grains.

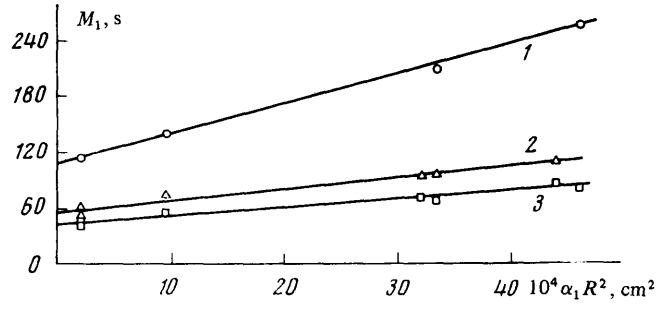


Figure 8. Moments of the kinetic curves (M_1) against $\alpha_1 R^2$; xenon on MSC-5A; 195 K; p = 0.8 kPa (*1*), 13.3 kPa (*2*), 26.6 kPa (*3*).

These expressions can be combined with the law of motion of the boundary to analyse experimental data on the adsorption kinetics of biporous adsorbents. In particular, it follows from Eqn. (41) that if the adsorption kinetics in the microporous regions are exponential and the characteristic time τ_a is not too great (more strictly, $\tau_a < R^2 a_0/2D_i c_0$) we can write

$$M_1 = \frac{\tau_i}{6} + \frac{2}{3}\tau_a\sqrt{\frac{2\tau_a}{\tau_i}}, \quad \tau_i = \frac{a_0}{c_0}\frac{R^2}{D_i}. \qquad (43)$$

The result of a gravimetric study of the adsorption kinetics of xenon by granules of active carbon of different size are illustrated in Fig. 8, where the first moments of the kinetic curves (M_1) are plotted against $\alpha_1 R^2$. α_1 is the shape factor of the granules. The moment of the kinetic function for the microporous regions $M_{\varphi 1}$ can be determined by extrapolation as the intercept on the vertical axis. We stress that Fig. 8 relates to the analytically more demanding situation of intermediate adsorption kinetics, when the characteristic diffusion times in the adsorption pores (τ_a) and in the transport pores (τ_i) are comparable. The integral of Eqn. (41) can be calculated from plots of $l(t)$ or $t_*(x)$ (Fig. 9), constructed from the radiographs of Fig. 7. The total moments M_1 calculated from Eqn. (41) agree with the experimental values.

The law of motion of the adsorption front $l(t)$, which can be determined for example by X-radiography, allows us to evaluate not only the integral characteristics of the kinetic function ($M_{\varphi k}$) but also the function $\varphi(t)$ itself. This involves solving the integral equation (37) with respect to $\varphi(t)$. The solution of this problem (inversion of the integral Laplace transform) is unstable towards small changes in the initial function $l(t)$, and therefore the experimental determination of $l(t)$ must be made with great care. This requirement is typical of the present

state of adsorption studies, with measurements of the microscopic properties of the adsorbent aimed not only at the integral properties of the adsorption process but also at its local characteristics (for example, as in this case, the distribution of adsorbate within the grain of adsorbent).

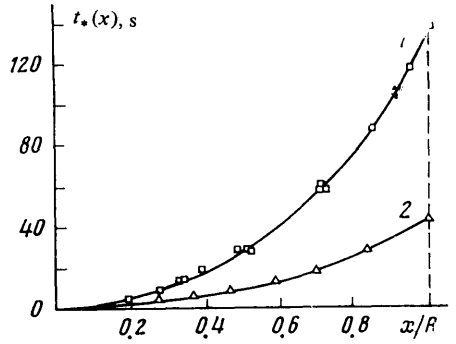


Figure 9. Plots of $t_*(x)$: p = 13.3 kPa (*1*) 26.6 kPa (*2*).

Work in our laboratory [25-40] and elsewhere [20-24] has shown that the bipore kinetic model offers some important advantages in the study of adsorption kinetics on real adsorbents, and in particular on formed zeolites. It gives a correct interpretation of the experimental results, free from the limitations of the classical quasi-diffusional model. However our model needs further experimental confirmation, particularly as regards the mechanism of mass transport in the microporous regions. The bipore model should ultimately lead to a rational choice of real adsorbents with the most favourable pore structure.

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