

The state properties of adsorbed fluids

Ondřej Kadlec

The Institute of Physical Chemistry and Electrochemistry
Czechoslovak Academy of Sciences, 182 23 Prague 8, Dolejškova 3

Abstract - The fundamental equation for the pressure of adsorbed fluids, containing the potential energy of the adsorbed molecule as a parameter, has been derived on the basis of the thermodynamics of fluids in the field of adsorption forces. As an example of its applicability, the state function of krypton adsorbed on the zeolite CaA has been evaluated. This function substantially deviates from that of the bulk krypton as a result of the smaller number of interacting atoms in the small volumes of adsorbate. On the basis of the state equations of adsorbed fluids, the equations of adsorption isotherms for energetically homogeneous adsorbents are derived. From these equations follows, that the shape of the isotherms in the coordinates amount adsorbed vs. logarithm of the equilibrium gas pressure, is determined by the state equation whereas its position on the abscissae axis depends on the potential energy of the adsorbed molecule in the adsorption space.

INTRODUCTION

The phenomenon of physical adsorption is caused by the enhancement of the density and concentration of fluids on the surfaces of solids or in micropores of solids, as a direct consequence of the existence of the attractive adsorption forces. This density is determined by the p^a, v^a, T state relation of a given adsorbed fluid. The pressure p^a of this fluid depends on the pressure p^g of the equilibrium gas existing outside the influence of adsorption forces and on the value of the potential of these forces, further denoted as ϕ . The relation between the above pressures and the potential ϕ can be evaluated by means of the general thermodynamical condition for equilibrium of fluids in the field of external forces with respect to the transport of matter firstly formulated by J.W. Gibbs. From the above ideas it is evident, that the theory of physical adsorption may be closely connected with the theory of state properties of fluids and eventually also with the extra complications in these properties caused by the presence of the surface of solid.

In the described treatment it is important to choose properly the concept of the structure of the adsorbed fluid. When the adsorbed fluid forms only a monolayer on the solid surface, the concept of the two-dimensional (2D) fluid should be chosen. The properties of this fluid can be described by 2D state functions such as the surface pressure π and the molar surface σ of the adsorbed fluid, etc. But when adjacently adsorbed molecules can take arbitrary positions in three dimensions with respect to each other, the three-dimensional (3D) concept of adsorbed fluid is to be applied and the 3D pressure p^a and the 3D molar volume v^a of the adsorbate should be introduced. The latter case concerns e.g. the adsorption of vapours in microporous solids, which will be mainly discussed in the present paper. There is an interesting correspondence between both concepts. As has been shown by E.A. Flood (ref. 1), they can be easily transformed into one another by a small change in the language.

Because in our treatment, the thermodynamics in the field of external forces is applied, the question of its applicability to adsorption phenomena should be elucidated. The basic assumption is, that the adsorbate behaves as a single component substance, remaining distinct and occupying separate and definite volumes (ref. 2). Then the important limitation of the scope of the Second Law of thermodynamics in small regions of colloidal systems

can be overcome by the interpretation of the state functions, such as pressure, temperature, volume, chemical potential etc., as time averaged quantities. Thus e.g. the physical meaning of the pressure p^a is the averaged force per unit area, which the molecules of the adsorbate on one side of the infinitesimal surface element exert on the other side. This averaging is clearly appropriate because of the macroscopic nature of the thermodynamic pressure, in contrast to the molecular dimensions of the surface regions. As a consequence, the Gibbsian condition for the equilibrium of the fluid, for every point of the adsorption space, where the potential energy of the adsorbed molecule is ϕ , may be written in the form

$$\mu^a(p^a, T^a) + \phi = \mu^g(p^g, T) \quad , \quad T^a = T = \text{const.} \quad , \quad (1)$$

where the state functions μ^a, p^a, T^a (μ^a is the chemical potential of adsorbed fluid and T^a is the temperature) represents the time averaged quantities. μ^g is the chemical potential of the equilibrium gas outside the influence of adsorption forces in the space, where the potential ϕ is zero. The relation between the pressures p^a and p^g of the adsorbed and equilibrium gas, respectively, important for the theory of physical adsorption, follows from the Gibbsian condition of equilibrium, as is clearly seen from its form (1), similarly as the relation between the surface pressure π and the gas pressure p^g can be evaluated from the Gibbsian adsorption equation. The explicit form of this $p^a(\phi, p^g)$ function is derived and its application in the analysis of the state properties of adsorbed fluids is demonstrated in the following chapters.

THE EQUATION FOR THE PRESSURE OF ADSORBED FLUIDS

As has been discussed above, the equation for the evaluation of the pressure p^a from the adsorption isotherm can be derived on the basis of equation (1). The chemical potentials μ^a and μ^g , which appears in this equation, depends on the corresponding pressures of the adsorbed and equilibrium gas. This dependence for the chemical potential of the liquid-like adsorbed fluid can be written in the form

$$\mu^a = \mu_0^1 + \int_{p_0^1}^{p^a} v^a dp^a + \mu^x \quad , \quad T = \text{const.} \quad , \quad (2)$$

where μ_0^1 and p_0^1 are the chemical potential and pressure, respectively, of the bulk liquid in the standard state at the temperature T and μ^x is the change in the chemical potential of the bulk liquid, when it is transferred in the adsorption space at the pressure p_0^1 . The chemical potential of equilibrium vapour at given temperature T is

$$\mu^g = \mu_0^g + \int_{p_0^g}^{p^g} v^g dp^g = \mu_0^g + RT \ln x + B(p_0^g - p^g) + \dots \quad (3)$$

where μ_0^g is the chemical potential of the vapour in the standard state, when its pressure is p_0^g , $x = p^g/p_0^g$ is the relative pressure of equilibrium vapour and B is the second virial coefficient of the Berliner form of the virial gas state equation.

Now we try to evaluate the molar volume v^a of adsorbed fluid by means of the adsorbed amount $a(x)$. When only the liquid-like or the gas-like fluid fill the volume V_0 of the adsorption space, in which the potential energy ϕ of the adsorbed molecule has a constant value, the molar volume v^a of this mobile fluid can be evaluated by the relation

$$v^a = V_0/a(x) \quad , \quad (4)$$

where $a(x)$ represents the so called full amount adsorbed at relative pressure x and is related to the experimentally measurable adsorbed amount $a_{\text{ex}}(x)$ by the relation

$$a(x) = a_{\text{ex}}(x) + (p^g V_0)/RT \quad , \quad (5)$$

Here it is important to emphasize, that the relation (4) is not generally valid. When the volume V_0 is partially filled by the adsorbed liquid-like fluid at negative p^a pressure and at the same time partially by the gas-

like fluid of positive p^{as} pressure, this relation is not valid. In this case eqn. (4) cannot be used for the evaluation of the value of the chemical potential μ^a according to the equation (2).

When we choose for convenience as standard that state of bulk vapour and liquid, where are in thermodynamical and mechanical equilibrium, when separated with flat interface ($\mu_o^g = \mu_o^l$ and $p_o^g = p_o^l$), then if the 3D vapour behaves as an ideal gas, by substituting equations (2)-(4) into the equilibrium condition (1) and by rearranging the obtained expression, the fundamental equation for the pressure p^a follows

$$p^a = \frac{RT}{V_o} \int_{\ln z}^{\ln x} a(x) d \ln x + p_o^l, \quad T = \text{const.}, \quad (6)$$

where p_o^l is the pressure of the bulk liquid in the standard state, equal to the normal saturated vapour pressure p_o^g at given temperature T and $z = \exp[(\phi + \mu^{\bar{x}})/RT]$ represents the relative pressure of equilibrium vapour, at which the adsorbed fluid pressure p^a is equal to the standard pressure p_o^l .

The equation (6) seems to be the 3D analog of the Gibbsian adsorption equation integrated according to Bangham (ref. 3)

$$\pi = \frac{RT}{S} \int_{\ln z = -\infty}^{\ln x} a(x) d \ln x, \quad T = \text{const.}, \quad (7)$$

where S is the specific surface of the adsorbent. It is frequently used for the evaluation of the surface pressure π . Moreover equation (6) contains the potential energy ϕ of the adsorbed molecule as parameter. This is connected with the reality, that equation (1) represents the condition of equilibrium containing chemical potentials in the integrated form. When the differential forms of the equilibrium condition are used in the evaluations of adsorbed fluid pressures (such as $du_a^g = d\mu^g$, cf. ref. 2), the potential energy ϕ is included in the integration constant, which disappears e.g. in the Bangham's treatment, in which it is assumed that the surface pressure is zero when the equilibrium gas pressure approach to zero.

When in an analogous derivation as presented here one chooses the arbitrary low pressure p_+^g of the gas as standard, one obtains for the pressure p^a the expression

$$p^a = \frac{RT}{V_o} \int_{\ln(zp_+^g)}^{\ln p^g} a(p^g) d \ln p^g + p_+^g, \quad T = \text{const.}, \quad (8)$$

which for $p_+^g \rightarrow 0$ yields the 3D analog of the integrated Gibbsian adsorption equation

$$p^a = \frac{RT}{V_o} \int_{\ln z = -\infty}^{\ln x} a(x) d \ln x, \quad T = \text{const.}, \quad (9)$$

where $z = \exp[(\phi + \mu^{\bar{x}})/RT]$ and $\mu^{\bar{x}}$ represent the change in the chemical potential of the gas, when it is transferred in the adsorption space at the pressure p_+^g .

The fundamental equation (6) for the pressure of the adsorbed fluid is consistent with the known relations valid in special situations. When the density of the adsorbed liquid does not depend appreciably on the pressure p^a , the mean value of the molar volume \bar{v}^{al} of the adsorbed liquid can be introduced in the relation (4). This relation when substituted in the rearranged form $\bar{a}(x) = V_o / \bar{v}^{al}$ in (6) yields the approximate expression for the pressure of the adsorbed liquid (cf. ref. 4)

$$p^{al} = [(RT)/\bar{v}^{al}] \ln(x/z) + p_o^l, \quad T = \text{const.}. \quad (10)$$

The potential energy ϕ in mesopores as well as $\mu^{\bar{x}}$ are zero. Hence, $z=1$ and the equation (10) is reduced to the well known expression for p^{al} from the theory of capillary condensation, i.e. $p^{al} = [(RT)/\bar{v}^{al}] \ln x + p_o^g$.

When we know the state equation of the adsorbed fluid, the pressure p^a can be evaluated without the knowledge of adsorption isotherm. The integral in the expression (2) for μ^a can be evaluated by means of this state function and by starting from eqns. (1)-(3) the explicit expression for $p^a(\phi, x)$, containing states parameters only, can be derived (ref. 5).

LIMITS OF APPLICABILITY OF THE EQUATIONS FOR THE PRESSURE p^a

It is important to realize that the equations (6), (8) and (9) cannot be successfully applied for evaluations of the pressures of adsorbed fluids from adsorption isotherms corresponding to adsorption processes in which the "phase transitions" with the metastable liquid-like fluid appear. This can be clearly demonstrated for the pressure p^a evaluated from the capillary condensation isotherm of vapour on a solid having cylindrical pores, all of radius r , open at one end, diagrammatically shown in Fig. 1.

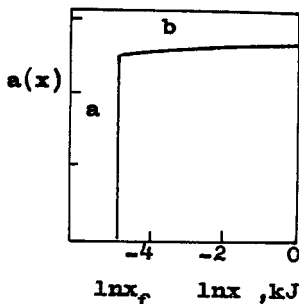


Fig. 1. Part a) represents the capillary condensation at the pressure $x=x_c$ and part b) represents the compression of condensed liquid corresponding to the increase of the negative pressure p^a , when the pressure x increases from $x=x_c$ to $x=1$. According to equation (6) for $x > x_c$, the evaluated pressure p^a yields a correct negative value approximately given by the equation $p^a = [(RT)/\bar{v}^{al}] \ln x$, in agreement with the theory of capillary condensation. The reason is, that in the pressure range $x_c > x > 1$, no phase transition occurs, i.e. pores are still volume filled by the

On the other hand the application of equation (9) yields erroneously the positive pressure p^a for the equilibrium relative pressure $x=1$. It is because in the gas pressure region from $x=0$ to $x=1$, the condensation of the gas-like to the liquid-like adsorbed fluid appears, in which the capillaries are filled by the condensed liquid existing in the metastable state ($p^a < 0$). It is evident that similar limitation of the applicability of the integrated Gibbsian adsorption equation (7) has to be taken into account, if the 2D metastable fluid can exist in the adsorption process. By not respecting the limits of applicability of the equation (4), or its 2D analog ($\sigma = S/a(x)$) the "effective character" of the evaluated equations of states of adsorbed fluids, described in the literature, can emerge. It should be also emphasized that all the equations (6)-(9) give correct values of the adsorbed fluid pressures only in cases, when the isotherms $a(x)$ correspond to an energetically homogeneous adsorbents. This is often not taken into account by many authors.

THE STATE RELATIONS OF ADSORBED FLUIDS

Equations (4), (6) and (9) enable to evaluate p^a, v^a, T state relations of the adsorbed fluid from adsorption isotherms. Such an evaluation for krypton is presented here as an example. The initial data taken from the paper of B.P. Bering at all (ref. 6) are redrawn in Fig. 2.

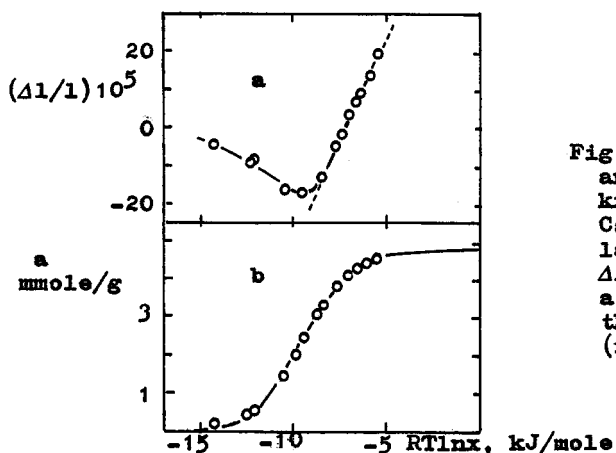


Fig. 2. Adsorption dilatometry and adsorption isotherms of krypton at 180 K on the zeolite CaA a) the dependence of the relative adsorbent granule length $\Delta l/l$, b) of the amount adsorbed $a(x)$, both on $RT \ln x$, redrawn from the paper of Bering at all (ref. 6).

As follows from Fig. 2a., at the $RT \ln z$ values ranging from -15 to -7.2 kJ mole $^{-1}$, the inequality $\Delta l/l < 0$ holds. Thus $p^a < 0$ and hence the adsorbed liquid-like krypton is in the metastable state. For this reason two different forms (6) and (9) of the equation for the pressure p^a have to be applied. When the adsorption volume V is completely volume filled by the liquid-like fluid, the rigorous value of p^a can be evaluated only by the eqn. (6). The value $V = 0.325$ cm 3 /g of the microcavities volume (ref. 7) and the value z given by the relation $RT \ln z = -7.2$ kJ/mole corresponding to $\Delta l/l = 0$ have been used in this evaluation together with the assumption that the potential energy ϕ of krypton atoms in the volume V is constant. Obviously this assumption is fulfilled only approximately. When at the low gas pressures x , the density of adsorbed krypton decreases so much, that it is reversibly converted into the gas-like state, equation (6) turns out not to be valid any longer. When the evaluation neglects this reality, the obtained state function has an effective character only. This is clearly seen from Fig. 3, where the real and the effective parts of the state function, evaluated by means of eqn. (4) and (6), are depicted by the full and the dotted curve 1, respectively, (the pressure of the gas-like fluid cannot be negative). On the other hand, in the range of small adsorbed amounts $a(x)$, the pressure p^a can be determined by eqn. (9) only. At higher adsorbed amounts, the evaluated state function again acquires the effective character in spite of the presence of the "phase transitions" with the presence of the metastable liquid-like fluid. This is illustrated in Fig. 3 by the full and dotted parts of the curve 2. The shape of the evaluated real state function $p^a(v^a)$ reminds the van der Waals state function. The hypothetical part with the positive slope $(\delta p^a / \delta v^a)_T$, joining both real branches of the state function, has been estimated by means of the Maxwell rule (curve 3).

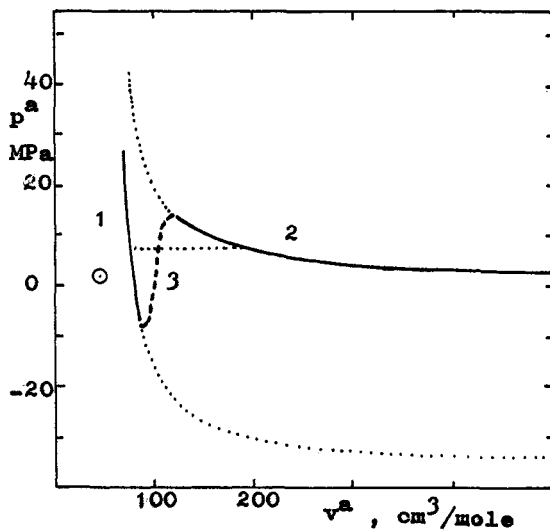


Fig. 3. The state $p^a(v^a)$ function of krypton adsorbed at 180 K on the zeolite CaA, evaluated by means of the eqns. (4), (6) and (9) from the experimental data shown on Fig. 2. The evaluated function strongly deviates from that for the bulk. The bulk standard state is denoted by e.

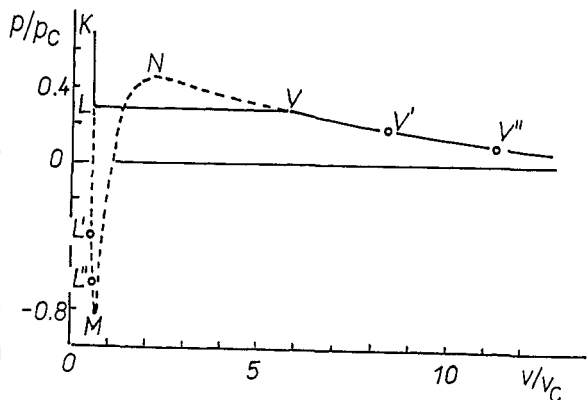


Fig. 4. the relation between pressure p and proper volume v of fluid below the critical temperature. The reversible "condensation" $V-L$, $V'-L$ and $V''-L''$ is shown diagrammatically.

Next we turn our attention to the mechanism of the transitions of gas-like to liquid-like adsorbed fluids. Because the micropores of zeolite CaA are volume filled by the metastable liquid-like krypton at negative p^a , this type of filling belongs to the second type of these mechanism (MVFM 2), the classification of which has been proposed recently (ref. 4). Here, the stress of the adsorbed liquid is caused by the bridging of the opposite walls of the zeolite cavities by the krypton liquid-like clusters and have nothing common with the classical theory of capillarity, because the surface of tension cannot be realized in the micropores. But when we overlook the presence of the field of adsorption forces, this process is formally analogous with reversible capillary condensation in one-side open

capillaries, discussed above. The "condensation" of such type can be illustrated diagrammatically on Fig. 4 as the transition from the state V' to the state L on the p, v, T diagram (for simplicity it is assumed that the $p^a(v^a, T)$ function is the same). This transition differs from the normal bulk fluid condensation under the equal vapour and liquid pressure ($p^g = p^l$), illustrated as the transition $V - L$. The reversible transition of the described type (e.g. $V'' - L''$) causes the effective character of the state functions, evaluated from the adsorption isotherms, when the adsorption space is filled according the MVFM 2.

THE CHANGES OF THE STATE EQUATION OF THE MATERIAL IN THE SMALL VOLUME OR LAYER OF THE ADSORBATE

As evident from Fig. 3, the state equation of adsorbed krypton contains another parameters, than that of the bulk fluid. The above conclusion is also supported by another result. The evaluation of the potential energy ϕ of the adsorbate may be performed by means of the rearranged Boltzmann function $\phi = RT \ln(p^{ag}/p^g)$, where the pressure p^{ag} , corresponding to given p^g is evaluated from the low pressure region of the adsorption isotherm by means of equation (9). The value ϕ for krypton on the zeolite CaA, evaluated in this way is -10.6 kJ/mole. On the other hand one has $RT \ln z = \phi + \mu = -7.2$ kJ/mole. As follows from these data, the value $\mu^* = 3.4$ kJ/mole of the perturbed chemical potential supports the idea, that the state equation of krypton largely deviates from that of the bulk fluid. As shown by A.W. Adamson (ref. 8), the perturbed chemical potential of the liquid-like fluid can be characterized by the relation $\mu^* = RT \ln(p_w/p_o^g)$, where p_w is the hypothetical pressure over the adsorbed fluid, remote from the field of forces, but not otherwise changed (its pressure $p^a = p^l$). From the determined value of μ^* it follows that the hypothetical pressure p_w is approximately ten times higher than the standard pressure of the bulk krypton. This result agrees well with the theoretical conclusions (ref. 9). The saturated pressure p_w of the vapour, which is in equilibrium with the liquid-like cluster of krypton atoms under the pressure p^l , is higher than the saturated pressure p^g of the bulk liquid in spite of the smaller number of interacting krypton atoms.

The smaller number of interacting atoms or molecules in the small volume of the adsorbate is the reason e.g. of the smaller value of the constant α of the van der Waals equation, as evident from the expressions that follow for the bulk and adsorbed van der Waals fluid (eqns. (11) and (12), respectively).

$$\alpha = \frac{N^2}{2} \int_d^{\infty} \frac{C_A}{r^6} 4\pi r^2 dr, \quad (11) \quad \alpha = \frac{N^2}{2} \int_d^D \frac{C_A}{r^6} 4\pi r^2 dr, \quad (12)$$

Here N is the Avogadro number, C_A the Kirkwood-Müller constant, diameter of the atom or the molecule and D is the diameter of the micropore cavity. The equation (12) is approximately valid, when the Law of intermolecular forces is the same in both cases (cf. ref. 10, 11). The critical temperature of fluids adsorbed in micropores is clearly substantially lower than the critical temperature of the bulk fluid, quite analogously to the case of 2D fluids.

ADSORPTION ISOTHERMS OF VAPOURS ON HOMOGENEOUS ADSORBENTS

When the relation (4) is quite correct and the equation of state of the adsorbed fluid is known, the equation of the adsorption isotherm can be evaluated on the basis of equations (1)-(4). Here the molar volume v^a of adsorbed fluid has to be the real state function and not a mean value corresponding to different fluid states in the separate parts of the adsorption volume V_0 . Further important assumption is, that the potential energy ϕ of the molecule is constant in any point of the adsorption space. For these conditions the derivation of equations of adsorption isotherms for the main state equations is derived. When we again choose the state of the bulk liquid and normal saturated vapour at given temperature T as standard and when we assume that the equilibrium gas behaves ideally, than the condi-

on (1) of the equilibrium can be expressed as follows

$$\int_{p_0}^{p^a} v^a dp^a + \phi + \mu^{\bar{x}} = RT \ln x \quad , \quad T = \text{const.} \quad (13)$$

because $\mu_0^1 = \mu_0^{\bar{g}}$ and $p_0^1 = p_0^{\bar{g}}$ holds. The integral on l.h.s. of this equation can be evaluated by means of the equations of state. The obtained $x(v^a, \phi)$ function can be transformed in the equation of adsorption isotherm by means of the relation (4).

(i) The virial adsorption isotherm

Now consider that the Leyden form of the virial state equation

$$\frac{p^a v^a}{RT} = 1 + \frac{A}{v^a} + \frac{B}{(v^a)^2} + \frac{C}{(v^a)^3} + \dots \quad (14)$$

describes well the p^a, v^a, T state relations of the adsorbed fluid. The evaluation of the integral of equation (13) by means of (14) may be performed per partes

$$\int_{p_0}^{p^a} v^a dp^a = \int_{p_0^1 v_0^1}^{p^a v^a} d(p^a v^a) - \int_{v_0^1}^{v^a} p^a dv^a \quad , \quad (15)$$

where v_0^1 is the molar volume of the bulk liquid in the standard state. From eqns. (13)-(15) the following equation of adsorption isotherm follows

$$x = \exp[(\phi + \mu^{\bar{x}})/RT] \Theta \exp\left[K + \frac{2A}{v_0^1} \Theta + \frac{3B}{2(v_0^1)^2} \Theta^2 + \frac{4C}{3(v_0^1)^3} \Theta^3 + \dots\right] \quad , \quad (16)$$

where

$$K = -\left(\frac{2A}{v_0^1} + \frac{3}{2} \frac{B}{(v_0^1)^2} + \frac{4}{3} \frac{C}{(v_0^1)^3} + \dots\right) \quad \text{and where} \quad \Theta = (av_0^1)/V_0 \quad .$$

(ii) The van der Waals adsorption isotherm

The adsorption isotherm for the v.d.Waals equation of state of the adsorbed fluid

$$\left(p^a + \frac{a}{(v^a)^2}\right)(v^a - b) = RT \quad (17)$$

is derived quite analogously as the virial isotherm on the basis of the equations (13), (15) and (17)

$$x = \exp[(\phi + \mu^{\bar{x}})/RT] \left(\frac{v_0^1}{b} - 1\right) \exp\left[\frac{-b}{v_0^1 - b} + \frac{2a}{RTv_0^1}\right] \frac{\Theta'}{1-\Theta'} \exp\left[\frac{\Theta'}{1-\Theta'} - \frac{2a}{bRT} \Theta'\right] \quad , \quad (18)$$

where $\Theta' = (ab)/V_0$. A similar but in form somewhat different equation of the isotherm has been derived by R.M.Barrer and A.B.Robins (ref. 9).

(iii) Adsorption isotherm of fluid described by the Amagat state equation

It is well known, that the state properties of many 2D fluids can be described with the Schofield-Rideal equation (ref. 10), which is the 2D analog of the Amagat state equation

$$p^a (v^a - v_b) = iRT \quad , \quad (19)$$

where v_b and i are constants. v_b is the covolume and i reflects the interaction between adsorbed molecules. From (13) and (19) one simply obtains the equation of the isotherm

$$x = \exp[(\phi + \mu^{\bar{x}})/RT] \left[\frac{1}{p_0^1} \left(\frac{iRTa}{v_0^1 - av_b}\right)\right]^i \exp\left[\frac{ia v_b}{v_0^1 - av_b} - \frac{p_0^1 v_b}{RT}\right] \quad , \quad (20)$$

where a is the adsorbed amount.

THE GENERAL PROPERTIES OF THE ADSORPTION ISOTHERMS

The adsorption isotherms of fluids in homogeneous field of adsorption forces, when expressed as functions of the amount adsorbed and of $RT \ln x$, can be separated into two parts, one of which is the potential energy ϕ and the other, $f(a)$ depends on the state properties of the adsorbed fluid only, i.e. the general equation can be written

$$RT \ln x = \phi + \mu^{\text{a}} + f(a), \quad (21)$$

where for the virial state equation (14) one has

$$f(a) = RT \ln(x/z) = RT \ln \theta + RT \left[- \sum_{i=1}^{\infty} \frac{i+1}{i} \frac{A_i}{(v_0^1)^i} + \sum_{i=1}^{\infty} \frac{i+1}{i} \frac{A_i}{(v_0^1)^i} \theta^i \right], \quad (22)$$

and where $A_1=A$, $A_2=B$, $A_3=C$...etc. For the v.d.Waals equation it follows

$$f(a) = k + RT \ln \left(\frac{\theta'}{1-\theta'} \right) + RT \left(\frac{\theta'}{1-\theta'} \right) - \frac{2a}{b} \theta', \quad (23)$$

where

$$k = RT \left[\ln \left(\frac{v_0^1}{b} - 1 \right) - \frac{b}{v_0^1 - b} \right] + \frac{2a}{v_0^1}. \quad (24)$$

For the Amagat state equation (19) describing the gas-like fluid

$$f(a) = RT \ln(x/z) = iRT \ln \left(\frac{iRTa}{v_0 - av_b} \frac{1}{p_0} \right) + \frac{iRTav_b}{v_0 - av_b} - p_0^1 v_b. \quad (25)$$

This is illustrated on the isotherms of krypton adsorbed at temperature $T=180$ K on the zeolites CaA and NaX, shown in Fig. 5.

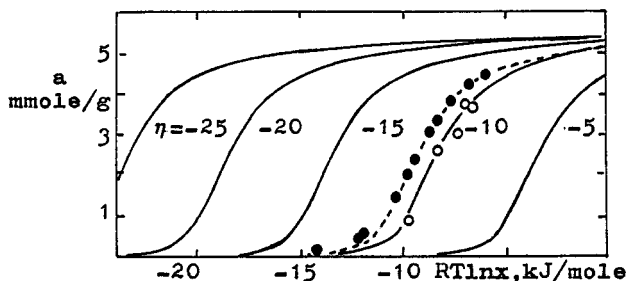


Fig. 5. The isotherm of krypton at $T=180$ K, evaluated by the eqn. (20) for different values of $\eta = \phi + \mu^{\text{a}}$ and $V=0.325$ cm³/g, $v_b=58.0$ cm³/mole and $i=0.5$. Experimental isotherms on the zeolite CaA (●) and NaX (○) are overtaken from the paper of B.P.Bering at all (ref. 6).

When we use the modified Amagat equation $(p^{\text{a}} - p_0)(v^{\text{a}} - v_b) = iRT$ for the state function₃ of liquid-like krypton (curve 1 in Fig.^m 3) having $p = -33.6$ MPa, $v_b = 58$ cm³/mole and $i=0.5$, the evaluated and experimental isotherms on CaA are in good agreement, when $\eta = \phi + \mu^{\text{a}} = -7.12$ kJ/mole. For gas-like krypton, the state function of which (curve 2 in Fig. 3) can be described by eqn. (19), $\mu^{\text{a}} = 0$ and $\eta = -10.95$ kJ/mole, as evident from the Fig. 5.

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