MODERN STATE OF THE THEORY OF GAS
AND VAPOUR ADSORPTION BY
MICROPOROUS ADSORBENTS

M. M. Dubinin

*Institute of Physical Chemistry, U.S.S.R. Academy of Sciences,
Moscow, U.S.S.R.*

One of the most important factors determining the nature of adsorption phenomena in the adsorption of gases and vapours by solids is the porous structure of the adsorbent. The peculiarity of adsorption phenomena on adsorbents which differ widely in their porous structure may be so great that it would be expedient to regard adsorption of a gas, on the smooth surface of a non-porous crystal and on an adsorbent with superfine pores (active carbons, zeolites) respectively, each as a phenomenon *sui generis* and to use entirely different model representations and calculation methods for their description.

It is convenient to divide the types of pores of adsorbents into three basic varieties according to the pore size. These varieties, which are characterized below, are most prominent in active carbons having a polymode volume distribution of pores.

(i) This class contains adsorbents having very large pores for which the curvature of the surface is negligibly small. Smooth surfaces may be regarded as a limiting case of such a porous structure. Therefore the upper limit of the radius of curvature of the surface of such pores is infinity. The lower limit of the curvature radius may be set conventionally at 1000–2000 Å. This selection of the lower limit means that volume filling of such pores by the mechanism of capillary condensation of vapour occurs only at relative pressures very close to unity. Therefore in conventional adsorption apparatus this phenomenon is practically indistinguishable from normal volume condensation corresponding to a plane meniscus. Thermodynamically, it is convenient to characterize such a porous structure by the value of the surface area *s* with no allowance for its curvature. Such pores will be termed "macropores".

(ii) This class is of smaller pores characterized by the fact that, besides the value of their surface area *s*, the curvature should be taken into account in many cases. The linear dimensions of such pores greatly exceed those of the adsorbate molecules. On the surface of these pores both mono-layer and multi-layer adsorption, *i.e.*, formation of successive adsorption layers on the surface, can occur. Besides this, in a certain, easily realized range of relative pressures, volume filling of these pores by the capillary condensation mechanism takes place. Somewhat tentatively, it may be assumed that the radii of curvature of the surface of such pores are within the range from 2000–15 Å. These pores will be termed "intermediate pores".
M. M. DUBININ

(iii) The third variety of pores, "micropores", is characterized by the following features. Their linear dimensions are below 10–15 Å, i.e., they are commensurate with those of the molecules of the adsorbed substances. The entire volume of micropores (as distinguished from transitional pores) represents a space where an adsorption field exists. It is well-known that the energy of adsorption, and hence the adsorption potentials in the micropores, are substantially increased in comparison with the corresponding values for adsorption both in transitional pores and on the surface of non-porous adsorbents of similar chemical nature. Since an adsorption field exists in the whole volume of micropores, and the concepts "surface" and "adsorption in layers" lose their physical meaning, it would be natural to consider that adsorption in micropores leads to their volume filling.

For certain porous crystals, for instance zeolites, whose microporous structure is strictly regular due to their crystalline structure, X-ray data enable the formal geometrical surface area of the aluminosilicate skeleton, i.e., "micropore walls" to be calculated. In the case of synthetic zeolites of the A and X type the formal geometrical surfaces of completely dehydrated crystals are $s = 1640 \text{ m}^2/\text{g}$ for CaA and $s = 1400 \text{ m}^2/\text{g}$ for NaX. There are no intermediate pores in zeolites, and the external surface areas of the crystals do not exceed 10 $\text{ m}^2/\text{g}$. The ratios of the calculated surface areas of zeolites to the conventionally used molecular areas of the adsorbed substances can be used as a measure of the volumes of the monomolecular adsorption layers $a_m$. In Table 1, these values are compared with the experimental maximum values of adsorption, $a_o$, corresponding to the total volume of the filling of the zeolite voids.

Table 1.

<table>
<thead>
<tr>
<th>Vapour</th>
<th>$t(°C)$</th>
<th>CaA ($s = 1640 \text{ m}^2/\text{g}$)</th>
<th>NaX ($s = 1400 \text{ m}^2/\text{g}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a_m$ (m mole/g)</td>
<td>$a_o$ (m mole/g)</td>
</tr>
<tr>
<td>Water</td>
<td>20</td>
<td>26.5</td>
<td>15.50</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>-196</td>
<td>16.2</td>
<td>8.61</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-196</td>
<td>16.8</td>
<td>8.27</td>
</tr>
<tr>
<td>Argon</td>
<td>-196</td>
<td>19.7</td>
<td>8.58</td>
</tr>
<tr>
<td>Benzene</td>
<td>20</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>20</td>
<td>7.53</td>
<td>2.26</td>
</tr>
</tbody>
</table>

According to Table 1, the calculated values, $a_m$, for monolayers greatly exceed the experimental maximum values of adsorption $a_o$. This example clearly shows the hopelessness and physical incompatibility of the conception of surface area of microporous adsorbents, i.e., adsorbents whose porous structure is made up of micropores.

It is worth noting that in colloid chemistry a similar question arises as to the lower limit of the linear sizes of colloidal particles, beyond which the concept of the interface between the dispersed phase and the dispersion medium loses its physical meaning. It is accepted that the lower limit of the sizes of colloidal particles is tentatively estimated at 10 Å and practically coincides with the lower limit of the sizes of transitional pores.

310
THEORY OF GAS AND VAPOUR ADSORPTION

Since the beginning of the development of the physical adsorption theory, two principal trends may be distinguished, one of which follows from the classical works of Langmuir and the other from Polanyi's investigations. The first is, as a rule, based on a detailed molecular model which makes it possible to obtain particular expressions for, or even numerical values of, the various parameters describing adsorption equilibrium. It is clear that even in the most favourable situations this type of adsorption theory is applicable only to idealized, usually very simple, models of the adsorbent. Whatever one's attitude towards the achievements in the modern theory of physical adsorption, which are based on simple idealized models, it is believed that attempts at applying such theories even to a semi-quantitative description of adsorption phenomena on real microporous adsorbents would be entirely hopeless.

Theoretical treatments of the second type, which are always more or less phenomenological, originate, as has already been agreed, from Polanyi's research. The originators of such treatments do not usually model all the details of adsorption interaction and the sorbent structure. This omission is however compensated for by the information usually obtained from adsorption experiments. If such information is reduced to a reasonable minimum and can be substantiated, at least in a general way, for instance, thermodynamically, then investigations conducted on this basis are usually fruitful and possess not only a descriptive, but also a predictive, force.

As is well-known, in his early works dedicated to the theory of adsorption, Polanyi made use of a function called the adsorption potential:

$$\epsilon = RT \ln \frac{p_0}{p}$$  \hspace{1cm} (1)

where $p_0$ is the pressure of the saturated vapour of the adsorbate at a temperature $T$; he showed experimentally that the $\epsilon/av$ curve (where $a$ is the value of adsorption at an equilibrium pressure $p$, and $v$ the molar volume of the adsorbate):

$$\epsilon = f(\alpha v)$$  \hspace{1cm} (2)

i.e., the so-called characteristic curve, is temperature-invariant for a given adsorbent-adsorbate system. In the course of further development of the theory it became evident that the interpretation of the function $\epsilon$ as the "adsorption potential" is physically invalid since it is tantamount to the statement that in the adsorbent pores there is an equipotential surface on which the adsorbate pressure is equal to $p_0$. It was therefore suggested that the function $\epsilon$ should be interpreted, not as the adsorption potential, but as a differential change of free energy $\Delta F$ (namely its decrease which is the differential maximal work of adsorption $A = -\Delta F$) during a reversible transfer of a mole of the adsorbate from a bulk liquid to an infinitely large amount of adsorbent. This means that the value $\epsilon$ is equal to the difference in the chemical potentials of the adsorbate in the state of bulk liquid and in the adsorbed state at one and the same temperature. In this definition:

$$A = RT \ln \frac{p_0}{p}$$  \hspace{1cm} (3)

$A$ does not mean the "adsorption potential" and it would therefore be quite
wrong to call the theory based on the properties of this function the “potential theory of adsorption”.

From Polanyi’s theory we use the statement that the characteristic adsorption curve:

\[ A = f(av) \]  \hspace{1cm} (4)

is temperature-invariant:

\[ P = \left( \frac{\partial A}{\partial T} \right)_{av} = 0 \]  \hspace{1cm} (5)

Thermodynamic arguments substantiating this assertion for microporous adsorbents will be cited below. The region of the fillings of the adsorption space where condition (5) is fulfilled will be termed the region of temperature invariance of \( A \).

The theory of physical adsorption of vapours and gases in micropores, which excludes the concepts of surface coverage and the formation of successive adsorption layers in micropores and assumes condition (5), \( i.e., \) the temperature invariance of the characteristic curve, will be referred to as the theory of volume filling of micropores. The present-day state of this theory will be described, together with its thermodynamical relationship to the theory of volume filling of transitional pores, \( i.e., \) the theory of capillary condensation of vapours in transitional pores.

It can be shown that the condition of temperature invariance of \( A \) [equation (5)], cannot, in principle, be fulfilled over the entire region of adsorption variations from \( a = 0 \) to the maximum value \( a_s \) at saturation, since there is a purely thermodynamic limitation of the temperature invariance region imposed by the same condition of temperature invariance of \( A \). This limitation is associated with the sign of differential molar entropy of vapour adsorption:

\[ \Delta S = \left( \frac{\partial A}{\partial T} \right)_{a} \]  \hspace{1cm} (6)

counted from the level of the entropy of a bulk liquid adsorbate at a given temperature.

The derivatives \( \left( \frac{\partial A}{\partial T} \right)_{a} \) and \( \left( \frac{\partial A}{\partial T} \right)_{av} \) have a thermodynamic relationship of a general nature:

\[ \Delta S = \left( \frac{\partial A}{\partial T} \right)_{a} = \left( \frac{\partial A}{\partial T} \right)_{av} + \alpha' \left( \frac{\partial A}{\partial \ln a} \right)_{T} \]  \hspace{1cm} (7)

in which

\[ \alpha' = \left( \frac{\partial \ln v}{\partial T} \right)_{A} > 0 \]  \hspace{1cm} (8)

represents, in a physical sense, the coefficient of thermal expansion of the adsorbed substance at a constant value of \( A \). It is obvious that this coefficient is a positive value. From equation (7) and the Gibbs–Helmholtz equation
a general expression for the differential molar heat of adsorption $Q$ is obtained:

$$Q = \lambda + A - T \left( \frac{\partial A}{\partial T} \right)_{av} - a' T \left( \frac{\partial A}{\partial \ln a} \right)_{T}$$  \hspace{1cm} (9)$$

where $\lambda$ is the heat of condensation of the adsorbate.

Returning to the analysis of equation (7), since $A$ is a decreasing function of the temperature for any type of adsorption isotherm, when the condition of invariance of $A$ is fulfilled, the differential entropy of adsorption should be negative$^4$, $^5$, $i.e.$:

$$\Delta S = \left( \frac{\partial A}{\partial T} \right)_{a} = a' \left( \frac{\partial A}{\partial \ln a} \right)_{T} < 0$$  \hspace{1cm} (10)$$

This inequality may be regarded as a thermodynamic criterion defining the upper limit of $A$, above which the existence of a temperature-invariance region is theoretically impossible. Proceeding from general thermodynamic considerations, it is easy to show that with a considerable decrease in adsorption $a$ the differential molar entropy of adsorption usually passes through zero and then becomes positive. Therefore the region of temperature invariance of $A$, expressed in terms of adsorption, will always be narrower than the whole range of changes of adsorption from zero to the maximum value $a_{m}$ at a relative pressure equal to unity.

It should be specially emphasized that the inequality $\Delta S < 0$ is necessary but insufficient to fulfill the condition of invariance of $A$. One of such examples is the phenomenon of capillary condensation of vapours in porous adsorbents, which also leads to the volume filling of much larger pores. For the filling of sorbent pores under conditions of complete wetting until spherical menisci of radius $r$ are formed, the following expression for the function $A$ may be obtained from the Kelvin equation:

$$A = RT \ln \frac{p_{m}/p}{\sigma} = \frac{2\sigma v}{r}$$  \hspace{1cm} (11)$$

where $\sigma$ is surface tension and $v$ is the molar volume of the adsorbate.

Substituting the expression for the derivative $(\partial A/\partial T)_{av}$ into the general equations (7) and (9) for the differential molar entropy of adsorption $\Delta S$ and the differential molar heat of adsorption $Q$, and assuming, naturally, that at a constant filling $av$ the meniscus curvature radius will be constant as well, the following expressions for the corresponding thermodynamic functions $\Delta S$ and $Q$ for capillary condensation of vapour are obtained:

$$\Delta S = A \frac{d \ln \sigma v}{dT} + a \left( \frac{\partial A}{\partial \ln a} \right)_{T}$$  \hspace{1cm} (12)$$

$$Q = \lambda + A - AT \frac{d \ln \sigma v}{dT} - a T \left( \frac{\partial A}{\partial \ln a} \right)_{T}$$  \hspace{1cm} (13)$$

When writing these expressions it is assumed that in the region where the Kelvin equation is valid, the temperature coefficient of the product $av$ for liquid in the sorbent pores is equal to the corresponding coefficient for bulk...
liquid. The values of the molar volume \( v \) and the coefficient of thermal volume expansion \( \alpha \) also correspond to bulk liquid.

As is well-known, the product \( \sigma v \) for liquids is a decreasing function of temperature, and therefore, in the light of equation (11):

\[
\left( \frac{\partial A}{\partial T} \right)_{sv} = A \frac{d \ln \sigma v}{dT} = Ak(T) < 0
\]  

(14)

In other words, in the region of capillary condensation of vapour, the derivative \( (\partial A/\partial T)_{sv} \) is negative and, hence, according to equation (12), the differential entropy of capillary condensation is negative, because the derivative \( (\partial A/\partial \ln a)_{T} \) is also negative. Thus, in the region of capillary condensation two conditions are necessary:

\[
\Delta S < 0 \text{ and } \left( \frac{\partial A}{\partial T} \right)_{sv} < 0
\]  

(15)

The second condition indicates the absence of temperature invariance of \( A \) for capillary condensation.

The above treatment makes it possible to assert that in the case of volume filling of the adsorption space of porous solids both by the mechanism of adsorption filling of micropores (active carbons, zeolites) and by the mechanism of capillary condensation in larger, i.e., intermediate pores (silica gels, alumina gels, etc.), the differential entropy of adsorption must be negative. This thermodynamic condition defines the upper limit of the values of \( A \), above which neither a region of temperature invariance of the characteristic curve for adsorption of vapour in micropores nor a region of capillary condensation of vapour in intermediate pores can exist.

It was shown by Hill\(^6\), in accordance with the BET theory of multi-layer adsorption, that at the most common value of the constant \( \varepsilon \approx 100 \) the differential entropy of adsorption becomes positive after the formation of approximately one statistical mono-layer. In a number of researches (e.g., Drain and Morrison\(^7\)) it has been shown experimentally that for adsorption of vapours on non-porous adsorbents there is a qualitative agreement between the curve "differential entropy of adsorption vs. filling" and Hill's theoretical curve. This suggests that multi-layer adsorption and capillary condensation, taken separately, are characterized by unlike signs of differential molar entropy of adsorption. This is shown schematically in Figure 1 where curve \( A \) is Hill's theoretical curve for \( \varepsilon = 100 \) and curve \( B \) is a curve for capillary condensation plotted in accordance with equation (12).

Equations (12) and (13) enable calculations of the differential molar heat \( Q \) and the differential molar entropy of adsorption \( \Delta S \) to be made for the region of capillary condensation of vapour from one isotherm, provided that the temperature dependence of the product of the surface tension and the molar volume for the bulk liquid is known. The results of the calculation of differential heat of adsorption as a function of the filling according to equation (13) are in good agreement with the isosteric heats of capillary condensation, as can be seen from Figure 2. In this figure the solid curve shows the dependence of \( Q \) on the filled volume of the sorption space, \( av \),
calculated from equation (13) using one experimental isotherm for the adsorption of benzene on comparatively fine-pore silica gel. The points indicate the values of the heat evolved obtained from isotherms measured directly for this system in our laboratory by Muminov.\(^8\) Equation (13) accurately describes the sharp maximum on the heat curve which is located in the intermediate vicinity of the maximal filling of the sorption volume. Such maxima, which were first noted by Goldmann and Polanyi,\(^9\) were later discovered calorimetrically in a number of investigations, for instance, by Beebe,\(^10\) Isirikian and Kiselev,\(^11\) Hodek and Julis\(^12\) and Muminov in direct measurements of isotherms of capillary condensation.

\[ Q, \text{kcal/mole} \]

\[ 0.05 \quad 0.10 \quad 0.15 \quad 0.20 \quad 0.25 \]

\[ av, \text{cm}^3/g \]

\[ \lambda \]

Figure 2. Relationship between the differential heat of adsorption \( Q \) of benzene on silica gel and the value of \( av \). The solid curve has been calculated by equation (13); values of \( Q \) found from the slope of adsorption isotherms.

Figure 3 (a), a more illustrative graphical representation of the above basic considerations, shows schematically two isotherms of adsorption at two different temperatures \( (T_2 > T_1) \) showing variation of free energy, \(-\Delta F\), vs. adsorption value, \( a \). Generally, adsorption will refer to either adsorption of vapour in micropores as such or capillary condensation of vapour in larger intermediate pores. From what has already been said, at a certain point \( B \) for which the variation of the differential molar entropy of adsorption is equal to zero, these curves should intersect, \( \Delta S > 0 \) lying to the left of the
point $B$, where the isotherm $T_2$ lies above the isotherm $T_1$, and $\Delta S < 0$ lying to the right of the point $B$, where the isotherm $T_2$ lies below the isotherm $T_1$. In Figure 3 (b) and (c) where the abscissa is $a$ rather than $a$, the points $A_1$ and $A_2$ merge into a single point $A$ which corresponds to the maximum filled volume of the adsorption or sorption space. When the isotherm $T_2$ in the interval AC (Figure 3 b) passes below the isotherm $T_1$, one has a typical case of capillary condensation, because, in the region $AC$ $(\partial A/\partial T)_a$ is obviously negative. When the isotherms coincide in the region $AC$ (Figure 3 c) this corresponds to adsorption in micropores where the condition of temperature invariance of $A$ is fulfilled, i.e., the partial derivative $P$ from the variation of free energy with temperature at a constant filled volume of the adsorption space $a$ is equal to zero. It is clear from Figure 3 that from

![Figure 3. Relative arrangement of adsorption isotherms at two temperatures ($T_2 > T_1$) in the coordinates $-\Delta F$ vs. $a$ and $-\Delta F$ vs. $av$](image)

the formal point of view the temperature invariance of the characteristic curve, $A = f(\omega)$, may be regarded as a limiting case of the arrangement of the isotherms in Figure 3 (b) where the derivative $P$ is equal to zero. All the factors causing the decrease of this derivative should enhance the tendency of the isotherms to converge in the region $AC$ of Figure 3 (b) and, consequently, lead to the temperature invariance of $A$. In this connection it is essential to establish the dependence of the derivative $P$ on $A$ for real systems.

As has already been shown, the derivative $P$ in a region where the Kelvin equation is valid is not only negative, but also proportional to the value of $A$ in equation (14). Figure 4 (a) exhibits the dependence of $P$ on $A$ plotted from the desorption branch of the isotherm of capillary condensation of benzene in the pores of dehydrated ferrous hydroxide gel according to the experiments of Lambert and Clark 18. In the temperature range studied (40–60°C) the product of the surface tension of benzene and the molar volume decreases linearly with temperature, and $k = d \ln \sigma /dT \approx 0.0041 \text{ deg}^{-1}$. The straight line $X$ in Figure 4 (a) is drawn at a slope theoretically equal to $k$. It is evident from the figure that as $A$ increases, the experimental values of the derivative $P$ first fall on the line $X$ and then, in the vicinity of the point $K$, sharply deviate from this line upwards and pass into the region of positive.
values of $P$. In the same figure, the values of the radii, calculated from the Kelvin equation, are also plotted along the abscissa. The point $K$ lies at approximately 16 Å and defines the limit of the values of $r$ below which the Kelvin equation is obviously invalid. Thus, the curve of Figure 4 (a) is remarkable in that it makes possible a thermodynamic determination of the lower limit of the applicability of the Kelvin equation.

![Figure 4. Dependence of derivative $P$ on $A$](image)

*Figure 4 (b) shows schematically the trend of the curve $P = \phi(A)$ for a more general case of the existence of the region of temperature invariance and the region of capillary condensation, as is observed, for instance, for active carbons with a developed intermediate porosity. In this case, as $A$ increases, i.e., as $p/p_0$ decreases from unity downwards, the first part of the graph is the linear interval $OA$ and then, in the region of temperature invariance, the curve coincides with the abscissa and, further on, passing over to small fillings, rises into the region of positive values of $P$ along $CD$. If the Ramsay–Shields equation is valid for a liquid adsorbate, then,

$$k \approx -\frac{1}{T_c - T}$$

Therefore for substances with higher values of $T_c$ the slope coefficient $k$ may be so small that this would lead to a satisfactory fulfilment from the practical point of view of the invariance condition in the entire region $OABC$.

The region $AB$ in Figure 4 (b) corresponds to transition to very small radii, i.e., to micropores for which the Kelvin equation becomes invalid. It would be expected that in this region the adsorption phase compressed in micropores by the action of the adsorption field would have a higher critical temperature as compared with a bulk liquid.

The increase in the critical temperature of the adsorption phase in the micropores follows from the fact that adsorption, defined as a Gibbs' excess (even at those values of adsorption at which one can consider the adsorption phase as condensed), does not vanish at the usual critical temperature $T_c$ but exists at $T > T_c^{14, 15}$. Thus, the difference between the gaseous and condensed adsorption phases does not disappear at $T = T_c$. This suggests that, in qualitative agreement with equation (16) for a condensed adsorption phase subjected to the action of an adsorption field in micropores, the
coefficient $K$ will be small or close to zero, thus corresponding approximately to the condition of invariance of the characteristic curve. If the volume of the micropores is relatively large, the adsorption isotherm should exhibit a protracted region $BC$ in Figure 4 (b) characterized by $K \approx 0$. If there are no micropores in the adsorbent, this region is altogether non-existent, which is illustrated schematically in Figure 4 (a). In the general case of an adsorbent having both intermediate and micropores, the relative extent of the regions of volume filling of pores $OA$ by the capillary condensation mechanism and $BC$ by the adsorption mechanism (Figure 4 b) is evidently determined by the structural peculiarities of the porous adsorbent.

Thus, in the adsorption of gases and vapours by microporous adsorbents there must exist a more or less extensive region of volume filling of micropores, which is characterized by temperature invariance of the characteristic curve. Given below is a brief outline of the most common, although in principle one particular, case of the theory of volume filling of micropores, describing adsorption equilibria in this region.

As a result of the analysis of numerous experimental data for the adsorption of the vapours of various substances on microporous adsorbents, especially carbonaceous ones, the following equation of a characteristic curve was suggested\textsuperscript{16} and substantiated theoretically\textsuperscript{17} for the temperature invariance region:

$$av^* = W_0 \left[ - \exp kA^2 \right] \quad (17)$$

where $W_0 = a_0v^*$ is a constant representing the maximum volume of the adsorption space (the micropore volume) and $v^*$ is the molar volume of the adsorbed substance. The second constant $k$ is the distribution parameter (dispersion) of the filled volume of the adsorption space with respect to the differential molar work of adsorption, $A$. Since the maximum volume of the adsorption space $W_0$ is independent of the nature of the vapour, it follows directly from equation (17) that for different vapours at constant filled volumes of the adsorption space $av^*$, the differential molar works of adsorption are related by the constant ratio:

$$\left( \frac{A}{A_0} \right)_{av^*} = \beta \approx \frac{P}{P_0} \quad (18)$$

\textit{i.e.,} $\beta$ is the affinity coefficient of the characteristic curve for the vapour under investigation. For carbonaceous adsorbents, the affinity coefficient is, as a good approximation, given by the ratio of the parachors of the substances, $P$.

As a result, the equation of the characteristic curve for any vapour will have the form:

$$av^* = W_0 \left[ - \exp k\frac{A^2}{\beta^2} \right] \quad (19)$$

Substituting into this equation the expression for the differential molar work of adsorption, the adsorption equation for vapour is obtained:

$$a = \frac{W_0}{v^*} \left[ - \exp B\frac{T^2}{\beta^2} \left( \log \frac{p_0}{p} \right)^2 \right] \quad (20)$$

318
THEORY OF GAS AND VAPOUR ADSORPTION

where $B$ is a constant, which is directly proportional to the distribution parameter $k$. This equation expresses the adsorption isotherm explicitly and the thermal equation of adsorption implicitly.

From the condition of constancy of the maximum volume of the adsorption space $W_0$, i.e., the micropore volume, it follows that for moderate temperatures the molar volumes of the adsorbed substances, $v^*$, are proportional to the molar volumes $v$ of the corresponding bulk liquids:

$$v^* = \gamma v$$  \hspace{1cm} (21)

The proportionality factor $\gamma$ is practically constant for the substances studied, within experimental error, and is probably close to unity. Methods for calculating molar volumes of adsorbed substances for higher temperatures, between the boiling points and the critical temperature$^{15, 18}$ have been developed and substantiated thermodynamically, and approximate expressions for $A$ and $v^*$ for the supercritical region, i.e., for the gaseous state of substances, have been obtained$^{15}$. As a result, for the case of microporous carbonaceous adsorbents the equations derived described fairly accurately the adsorption equilibrium for many classes of substances in broad intervals of fillings of the adsorption space. This theory can also be applied with advantage to microporous mineral adsorbents (very fine-pore gels, porous glasses) and in a number of cases to zeolites. Recently the first successful steps were made with the aim of generalizing the theory to the case of adsorption of a binary mixture of vapours on microporous adsorbents$^{19}$.

For the temperature invariance region, the equations (7) and (9) for the variation in the differential molar entropy of adsorption $\Delta S$ and in the differential heat of adsorption $Q$ acquire the following form$^{20}$:

$$\Delta S = \alpha' RT \left( \frac{\partial \ln \rho_b}{\partial \ln a} \right)_T$$  \hspace{1cm} (22)

and

$$Q = \lambda + A - \alpha' RT^2 \left( \frac{\partial \ln \rho_b}{\partial \ln a} \right)_T$$  \hspace{1cm} (23)

Of course, these equations are independent of the form of the characteristic curve equation and enable these thermodynamic functions to be calculated from a single adsorption isotherm. On the other hand, if the characteristic curve and, accordingly, the adsorption isotherm are described by equations (19) and (20), these expressions may be represented as:

$$\Delta S = - \frac{2.3a\beta R}{2B^4} \left( \ln \frac{W_0}{av} \right)^{-\frac{3}{2}}$$  \hspace{1cm} (24)

$$Q = \lambda + \frac{2.3\beta R}{B^4} \left[ \left( \ln \frac{W_0}{av} \right)^{\frac{3}{2}} + \frac{aT}{2} \left( \ln \frac{W_0}{av} \right)^{-\frac{1}{2}} \right]$$  \hspace{1cm} (25)

For moderate temperatures it is possible, as a good approximation, to take the molar volume of the adsorbed substance as equal to the molar volume of the corresponding bulk liquid, and to consider that the coefficient $\alpha'$ in equations (22) and (23) is numerically equal to the coefficient of thermal expansion of the bulk liquid, $a$.

P.A.C.—C

319
Differential heats of adsorption $Q$ calculated from equation (25) and determined experimentally for a number of systems studied are, as a rule, in good agreement. By way of illustration, Figure 5 shows $Q/a$ curves for benzene on active carbons with different microporous structures obtained by Dubinin and Polstyanov. The solid curves have been computed from the constants $W_0$ and $B$ of the adsorption isotherm equation (20), and the circles show the experimental values of $Q$ determined from the adsorption isosteres. The upper curve demonstrates the best agreement of the theoretical and experimental results, while the lower shows the worst agreement; in the latter case the divergency does not exceed 5 per cent.

![Figure 5](image)

*Figure 5. Relationship between the differential heat of adsorption $Q$ of benzene on active carbons and the value of adsorption $a$. The solid curves have been calculated according to equation (25); values of $Q$ have been found from the slopes of the adsorption isosteres.*

It would be wrong to think that the theory of physical adsorption of gases and vapours by microporous adsorbents, briefly outlined here, can claim the role of a universal theory of physical adsorption. Its application is restricted to the region of temperature invariance of a characteristic curve and it is therefore only suitable for describing adsorption in micropores. However, the theory of volume filling of micropores stands out among the majority of the known theories of adsorption in that it provides computation facilities which make it possible, by the use of a few readily determinable characteristics of the adsorbent and the adsorbate, to calculate adsorption isotherms over a wide temperature range, as well as the basic thermodynamic characteristics of adsorption equilibrium, $\Delta S$ and $Q$, for a large number of substances and the important real microporous adsorbants, subject to the above-mentioned limitations. Thus, within the framework indicated, the theory of volume filling solves the basic problem facing the theory of physical adsorption, i.e., the quantitative description and calculation of the parameters of the adsorption equilibrium of various substances on real microporous adsorbents. Nevertheless, we clearly realize that the improvement and development of the concepts presented here will require further theoretical and experimental research.
THEORY OF GAS AND VAPOUR ADSORPTION


References