

THEORY OF VOLUME FILLING FOR VAPOR ADSORPTION

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ABSTRACT

A rational classification of adsorbent pores by size is suggested. It is shown that for the finest pores (micropores, radii $r \lesssim 15$ Å) adsorption follows the mechanism of volume filling of the adsorption space rather than the mechanism of surface coverage, i.e., formation of successive layers. In larger pores (intermediate pores, $15 \lesssim r \lesssim 1000$ Å), when the relative pressures are sufficiently high, adsorption in layers on the surface turns into volume filling by the capillary condensation mechanism. Thermodynamic equations for differential entropy and heat are derived which are valid for both cases of volume filling of pores. The fundamental principles of the theory of physical adsorption of vapors in micropores, which consist in the concept of volume filling of these pores and the zero value of the derivative

$$[\partial RT \ln (p_s/p)/\partial T]_{av} = P,$$

are discussed. These concepts make it possible to regard adsorption in micropores as a limiting case of volume filling corresponding to negligible, practically zero, values of P . Arguments are adduced in favor of the fact that the value of P in micropores should actually tend to zero. In volume filling of both intermediate pores and micropores, differential entropy of adsorption, $\Delta S = [\partial RT \ln (p_s/p)/\partial T]_a$ is negative. The thermodynamic difference of these two phenomena consists in the fact that for capillary condensation $P < 0$, whereas for adsorption filling of micropores $P = 0$.

The case of the theory of volume filling of micropores where the characteristic curve is given by the equation $av = W_0 \exp [-D(RT \ln p_s/p)^2]$ is considered.

One of the most important factors determining the nature of adsorption phenomena in adsorption of gases and vapors by solids is the porous structure of the adsorbent. The peculiarity of adsorption phenomena on adsorbents widely differing in their porous structure, may be so great that it would be expedient to regard adsorption of a gas, for instance, on the smooth surface of a nonporous crystal and on an adsorbent with superfine pores (of the type of active carbon or zeolite) as phenomena sui generis and to use entirely different model representations and different calculation methods for their description.

It is convenient to divide all the diverse types of pores of adsorbents in accordance with the views presented below into three basic varieties depending on the pore size.

1. Large pores for which the curvature at any point of the surface is

negligibly small. Smooth surfaces may be regarded as a limiting case of such a porous structure. The upper limit of the curvature radius of the surface of such pores $r_{max} = \infty$; the lower limit may be set conventionally at $r_{min} \approx 500\text{--}1,000$ Å. This selection of the lower limit means that volume filling of such pores by the capillary condensation mechanism occurs only at relative pressures so close to unity that 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. We shall call pores of this type macropores.

2. Smaller pores, for which besides the surface area often the curvature should be considered. For such pores, as for macropores, the linear dimensions characterizing them may be considered to exceed by far those of the adsorbate molecules. On the surface of these pores occurs monolayer and multilayer adsorption, i.e., formation of successive layers on the surface. 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 curvature radii of the surface of such pores are within the range $500\text{--}1,000 \gtrsim r \gtrsim 15$ Å. We shall term pores of this type intermediate pores.

3. The third variety of pores, to which we shall refer as micropores, is characterized by the following features. The linear dimensions of these pores $r < 10\text{--}15$ Å, i.e., they are commensurable with those of the molecules of usual adsorbates. In a number of cases micropores are inaccessible to molecules of certain adsorbates for sterical reasons. For such pores it is quite difficult to define the concept "surface area;" in any case up to now nobody has succeeded in doing so and in indicating some experimental method for measuring this value. The entire volume of micropores (as distinguished from transitional pores) represents a space where an adsorption field exists. At any point of this space adsorption potentials set up by "the opposite walls of the pores" are superposed on each other. Since an adsorption field exists in the whole volume of such pores and the concepts "surface" and "adsorption in layers" lose their definite meaning, it would be natural to expect that adsorption in such pores should lead to their volume filling.

It should be emphasized that such a systematic classification of the pores of sorbents by no means implies that it is simultaneously the classification of the sorbents themselves. On the contrary, as a rule, one and the same adsorbent may contain pores of all the three types. Therefore a comprehensive description of adsorption on a particular real sorbent should include the peculiarity of phenomena in all pore varieties. In practice, however, we often encounter sorbents where only one of the pore varieties is especially

well developed (for instance, micropores in the case of microporous sorbents). Besides, phenomena typical, for example, of volume filling of micropores and intermediate pores largely occur in different intervals of equilibrium pressures. Therefore attempts to consider independently adsorption phenomena in different pore varieties are completely justified. The foregoing classification of pores, which, by and large, is of general nature, is particularly convenient when applied to active carbons with a polymode volume distribution of pores according to their radii (1). For such adsorbents these three pore varieties are manifested especially clearly on differential pore-volume distribution curves.

Since the very first years of development of the physical adsorption theory, two principal trends are distinguished, one of which follows from the classical works of Langmuir and the other of which follows from Polanyi's investigations. The first trend 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 of adsorption equilibrium. It is clearly evident that even in the most favorable situations this type of adsorption theory is applicable only to idealized, usually very simple models of the adsorbent and of the nature of adsorption interaction. 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 semiquantitative description of adsorption phenomena on real microporous adsorbents would be entirely hopeless.

Theoretical works of the second type, which are always more or less phenomenological, originate, as has already been said, from Polanyi's research. The authors of such works usually do not resort to modeling all the details of adsorption interaction and the sorbent structure. This omission is compensated for by phenomenological information ordinarily obtained from adsorption experiments. If such information, on the one hand, is reduced to a reasonable minimum and, on the other, 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 we see it, the study of physical adsorption on real microporous sorbents has led to the greatest successes precisely in this direction, and such theories should be developed and perfected.

As is well known, in his early works dedicated to the theory of adsorption, Polanyi made use of the function $\epsilon = RT \ln p_s/p$ (where p_s is the pressure of the saturated vapor of the adsorbate at a given temperature T), which is called the adsorption potential, and he showed experimentally that the ϵ vs. av curve (where a is adsorption and v the molar volume of the adsorbate), i.e., the so-called characteristic curve, is temperature-invariant for a given adsorbent-adsorbate system. In the course of further develop-

ment of the theory it became evident that the interpretation of the value ϵ 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_s . Therefore it was suggested long ago that the function ϵ should be interpreted, not as the adsorption potential, but as a differential change of free energy ΔF during a reversible isothermal transfer of a mole of the adsorbate from a bulk liquid to an infinitely large amount of adsorbent. This means that the value ΔF 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 of the function ΔF it does not acquire the meaning of the "adsorption potential," and therefore it would be quite improper to assign the name of the "potential theory of adsorption" to the theory of adsorption based on the properties of this function.

From Polanyi's theory we borrow only the statement that the function $\Delta F = f(av)$ is temperature-invariant, i.e., that

$$P \equiv (\partial \Delta F / \partial T)_{av} = 0. \quad [1]$$

We shall attempt to adduce thermodynamical arguments substantiating this assertion for microporous sorbents. The region of the characteristic curve where condition [1] is fulfilled will be termed the region of temperature invariance of ΔF .

The theory of physical adsorption of vapors (and gases) in micropores, which excludes the concept of the surface coverage and formation of successive adsorption layers in such pores and accepts condition [1], will be referred to as the theory of volume filling of micropores. Below we shall describe the present-day state of this theory and its thermodynamical relationship with the theory of volume filling of transitional pores (theory of capillary condensation).

It can be demonstrated that condition [1], in principle, cannot be fulfilled in the entire region of adsorption variations from $a = 0$ to the maximum value a_s at saturation, since there is a purely thermodynamical limitation of the temperature-invariance region imposed by the same condition [1]. This limitation is associated with the sign of differential molar entropy of vapor adsorption $\Delta S = (\partial \Delta F / \partial T)_a$ counted from the level of the entropy of a bulk liquid adsorbate at a given temperature.

The derivatives $(\partial \Delta F / \partial T)_a$ and $(\partial \Delta F / \partial T)_{av}$ are bound by a thermodynamical relationship of a very general nature. Indeed, if it is assumed that in one case a is a function of ΔF and T , and that in another av is a function of the same independent variables,

$$\phi(a, \Delta F, T) = 0; \quad [2]$$

$$\psi(av, \Delta F, T) = 0. \quad [3]$$

By determining the derivative $(\partial a/\partial T)_{\Delta F}$ from Eq. [2], substituting it into the expression for the derivative $(\partial \Delta F/\partial T)_{av}$ from Eq. [3] and making the necessary transformations we obtain the sought relation:

$$\left(\frac{\partial \Delta F}{\partial T}\right)_a = \left(\frac{\partial \Delta F}{\partial T}\right)_{av} + \left(\frac{\partial \ln v}{\partial T}\right)_{\Delta F} \left(\frac{\partial \Delta F}{\partial \ln a}\right)_T. \quad [4]$$

The derivative $(\partial \ln v/\partial T)_{\Delta F}$ in this equation, which is evidently positive, represents in a physical sense the coefficient of thermal expansion of the adsorbed substance at a constant value of ΔF :

$$\alpha' = \left(\frac{\partial \ln v}{\partial T}\right)_{\Delta F} > 0. \quad [5]$$

Therefore, instead of Eq. [4] we obtain

$$\Delta S = \left(\frac{\partial \Delta F}{\partial T}\right)_a = \left(\frac{\partial \Delta F}{\partial T}\right)_{av} + \alpha' \left(\frac{\partial \Delta F}{\partial \ln a}\right)_T. \quad [6]$$

Substituting this value of ΔS into the Gibbs-Helmholtz equation

$$Q = \lambda + \Delta F - T\Delta S, \quad [7]$$

where λ is the heat of condensation of the adsorbate, we find a general expression for the differential molar heat Q of adsorption

$$Q = \lambda + \Delta F - T \left(\frac{\partial \Delta F}{\partial T}\right)_{av} - \alpha' T \left(\frac{\partial \Delta F}{\partial \ln a}\right)_T. \quad [8]$$

The second term in the right-hand side of Eq. [6] for any type of isotherm of adsorption is negative because ΔF is always a decreasing function of a . Owing to this, when condition [1] is fulfilled, differential entropy of adsorption should be negative¹ as was shown by us previously (2, 3), i.e.,

$$\Delta S = \left(\frac{\partial \Delta F}{\partial T}\right)_a = \alpha' \left(\frac{\partial \Delta F}{\partial \ln a}\right)_T < 0. \quad [9]$$

In calculations by Eqs. [8] and [9] as well as by equations following from them and given later, it is possible, as a rule, to assume that α' is numerically equal to the coefficient of thermal expansion of a bulk liquid $\alpha = d \ln v/dT$. The inequality [9] may be regarded as a thermodynamical criterion defining

¹ The statement of J. P. Hobson and R. A. Armstrong (*J. Phys. Chem.* **67**, 2000 (1963)), that for adsorption of Ar and N_2 on Pyrex glass at very low pressures the temperature invariance of the characteristic curve and the condition $\Delta S = 0$, are fulfilled simultaneously, is based on a misunderstanding. Hobson and Armstrong suppose that the temperature invariance of the characteristic curve may be written in the form $(\partial \Delta F/\partial T)_a = 0$ rather than $(\partial \Delta F/\partial T)_{av} = 0$. From our equation [6] it is obvious that if $(\partial \Delta F/\partial T)_a = 0$ (i.e., if the differential entropy is equal to zero) the derivative $(\partial \Delta F/\partial T)_{av}$ is positive; therefore in this case the Polanyi theory is inapplicable because our equation [1] is not fulfilled.

the upper limit of ΔF above which the existence of a temperature-invariance region is impossible in principle. Since a decrease in adsorption a to zero causes Q to tend to some finite value, and ΔF grows indefinitely at $p \rightarrow 0$, then, as follows from Eq. [7], ΔS passes zero at a certain value of a and further becomes positive, and at $a \rightarrow 0$ also grows indefinitely. On these grounds one can state that for any isotherm of adsorption there exists a region where $\Delta S > 0$, and therefore the region of temperature invariance will always be narrower than the whole range of changes of a from 0 to a_s .

It should be specially emphasized that the condition $\Delta S < 0$ is necessary but insufficient to fulfill condition [1], for a number of cases may be quoted where $\Delta S < 0$ but where the condition of temperature invariance is not met. One of such examples is the phenomenon of capillary condensation of vapors in porous sorbents.

Indeed, under conditions of complete wetting, the following expression may be written in accordance with the Kelvin equation for a spherical meniscus of radius r :

$$\Delta F = RT \ln p_s/p = 2\sigma v/r, \quad [10]$$

where σ is the surface tension and v is the molar volume of the adsorbate. At a constant degree of filling of the adsorption space, i.e., at $av = \text{const.}$, the curvature radius of the meniscus is also constant, i.e., $r = \text{const.}$, and therefore

$$\left(\frac{\partial \Delta F}{\partial T}\right)_{av} = \frac{2}{r} \left(\frac{\partial \sigma v}{\partial T}\right)_{av} = \Delta F \left(\frac{\partial \ln \sigma v}{\partial T}\right)_{av} = \Delta F \frac{d \ln \sigma v}{dT}. \quad [11]$$

We also assume that in the region where the Kelvin equation [10] is valid, the temperature coefficient of the product σv for liquid in capillaries is equal to the corresponding coefficient for bulk liquid. Substituting $(\partial \Delta F / \partial T)_{av}$ from Eq. [11] into Eqs. [6] and [7], we obtain the following expressions for differential entropy and differential heat of capillary condensation:

$$\Delta S = \Delta F \frac{d \ln \sigma v}{dT} + \alpha \left(\frac{\partial \Delta F}{\partial \ln a}\right)_T; \quad [12]$$

$$Q = \lambda + \Delta F - \Delta F \cdot T \frac{d \ln \sigma v}{dT} - \alpha T \left(\frac{\partial \Delta F}{\partial \ln a}\right)_T. \quad [13]$$

As is well known, the product σv for liquids is a decreasing function of temperature, i.e.,

$$\frac{d \ln \sigma v}{dT} = K(T) = \frac{d \ln \sigma}{dT} + \frac{d \ln v}{dT} = \gamma + \alpha < 0; \quad [14]$$

and therefore

$$\left(\frac{\partial \Delta F}{\partial T}\right)_{av} = \Delta F \frac{d \ln \sigma v}{dT} = \Delta F K < 0. \quad [15]$$

In other words, in the region of capillary condensation the derivative $(\partial\Delta F/\partial T)_{av}$ is negative and, hence, the differential entropy of capillary condensation is also negative, because $(\partial\Delta F/\partial \ln a)_T < 0$. Thus, in the region of capillary condensation two conditions are necessary:

$$\Delta S < 0 \quad \text{and} \quad (\partial\Delta F/\partial T)_{av} < 0. \quad [16]$$

Consequently we can 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 pores (silica gels, alumina gels, etc.) differential entropy of adsorption must be negative. In both cases [9] and [12] this purely thermodynamical condition is necessary, although insufficient, for the formation of a condensed volume phase in the pores of a solid, and it defines the upper limit of the values of ΔF above which neither a region of temperature invariance nor a region of capillary condensation can exist.

It was shown by Hill (4) within the framework of the BET theory of multilayer adsorption that after the formation of approximately one statistical monolayer differential entropy of adsorption becomes positive (at least for the most common value of the constant $c \approx 100$), as is pictured schematically in Fig. 1 (curve 1). In a number of works (see, for example, reference 5), it was found experimentally that for adsorption on nonporous adsorbents a qualitative agreement of the curve $\Delta S = f(a)$ with Hill's theoretical curve is observed. This suggests that multilayer adsorption and capil-

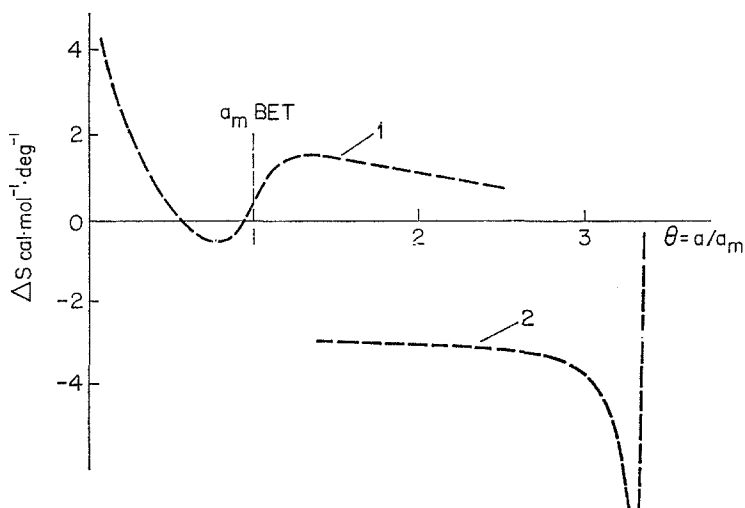


FIG. 1. Variation in differential entropy ΔS of adsorption with filling. Curve 1—multilayer adsorption after Hill (4) at $c \approx 100$. Curve 2—capillary condensation according to Eq. [12] (reference 8).

lary condensation, taken separately, are characterized by unlike signs of ΔS , as shown schematically in Fig. 1, where curve 1 shows the dependence of ΔS on a according to Hill for multilayer adsorption, and curve 2, the corresponding dependence for capillary condensation in accordance with Eq. [12].

Equations [12] and [13] permit calculation of Q and ΔS for the region of capillary condensation from one isotherm of adsorption provided that the temperature dependence of σv is known. In a special case, when condition [1] is fulfilled, Eqs. [6] and [8] are transformed into the corresponding equations

$$\Delta S = \alpha \left(\frac{\partial \Delta F}{\partial \ln a} \right)_T = \alpha R T \left(\frac{\partial \ln p_s/p}{\partial \ln a} \right)_T \quad [17]$$

$$Q = \lambda + \Delta F - \alpha T \left(\frac{\partial \Delta F}{\partial \ln a} \right)_T = \lambda + \Delta F - \alpha R T^2 \left(\frac{\partial \ln p_s/p}{\partial \ln a} \right)_T \quad [18]$$

derived by us previously (6), which permit calculation of ΔS and Q from one isotherm of adsorption for the region of temperature invariance of ΔF .

Equation [13] is equivalent to Hückel's equation (7) which is the more complicated and less amenable to calculation. This equation is derived by him for the heat of capillary condensation:

$$Q = \lambda + \frac{2v}{r} \left(\sigma - T \frac{d\sigma}{dT} \right) + \frac{2\sigma T}{r} \left(\frac{\partial v}{\partial T} \right)_a + \frac{2\sigma a T}{r} \left(\frac{\partial v}{\partial T} \right)_r \left(\frac{\partial \ln r}{\partial a} \right)_T. \quad [19]$$

The identity of Eqs. [13] and [19] can be demonstrated by means of suitable transformations. It should be noted that the results of calculations of Q from Eq. [13] are in good agreement with the experimental isosteric heats of adsorption, as can be seen from Fig. 2. In this figure the solid curve

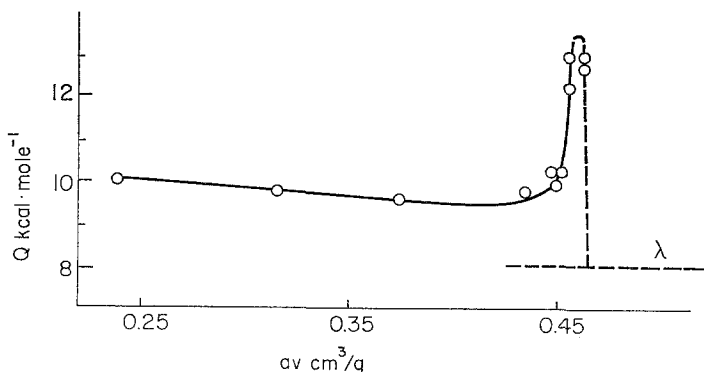


FIG. 2. Relationship between differential heat of adsorption Q of benzene on silica gel and the value of av . The solid curve has been calculated by Eq. [13]; \odot —values of Q found from the slope of isosteres of adsorption.

shows the dependence of Q on av calculated from Eq. [13] using one experimental isotherm of adsorption of benzene on silica gel, and the points indicate the values of heat obtained from isosteres of adsorption measured directly in our Laboratory for this system by S. Z. Muminov (8). Equation [13] accurately describes the sharp maximum on the heat curve which is located in the immediate 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 (10, 11) and also found in direct measurements of isosteres of adsorption (8, 12).

For convenience in further discussion, we illustrate graphically some of the considerations adduced before. Figure 3a shows schematically two isotherms of adsorption at two different temperatures ($T_2 > T_1$), in coordinates a , ΔF . At a certain point B (where $\Delta S = 0$) these isotherms should intersect, $\Delta S > 0$ being to the left of point B , where the isotherm T_2 lies above the isotherm T_1 , and $\Delta S < 0$ being to the right of point B , where the isotherm T_2 lies below the isotherm T_1 . When changing to coordinates av , ΔF all the abscissas of the isotherm T_2 should be multiplied by v_2 , and accordingly the abscissas of the isotherm T_1 by v_1 , the value of v_2 being larger than v_1 since α is positive. With this transformation of the coordinates (see Figs. 3b and c), the points A_1 and A_2 should coincide at the point A which corresponds to the maximum volume $a_v v$ of the adsorption space. If the isotherm T_2 in the interval AC in Fig. 3b passes below the isotherm T_1 , we shall have a case typical of capillary condensation, because, in the region AC , $(\partial \Delta F / \partial T)_{av}$ is obviously negative. If, in a particular case, the two isotherms coincide in the region AC in Fig. 3c, we have temperature invariance of ΔF , i.e., $(\partial \Delta F / \partial T)_{av} = 0$.

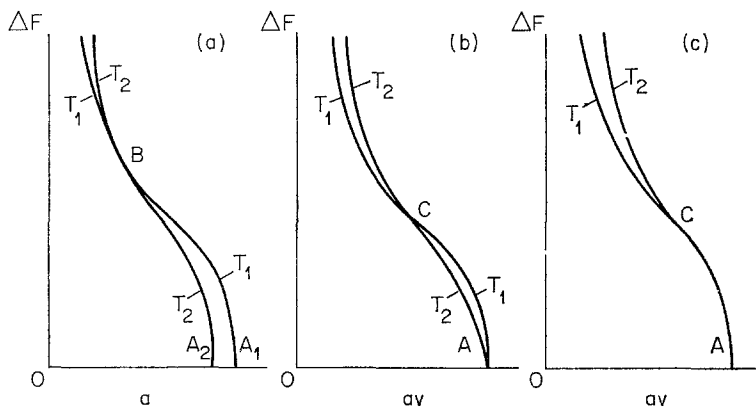


FIG. 3. Relative arrangement of isotherms of adsorption at two temperatures ($T_2 > T_1$) in the coordinates ΔF , a , and ΔF , av .

It is clear from Fig. 3 that from the formal point of view we may regard the temperature invariance of the characteristic curve $\Delta F = f(av)$ as a limiting case of the arrangement of the isotherms of Fig. 3b in which $(\partial\Delta F/\partial T)_{av}$ vanishes to zero. All the factors causing this decrease should enhance the trend of the isotherms to draw together in the region AC and, consequently, aid in the realization of condition [1]. In this connection it is essential to establish the dependence of $(\partial\Delta F/\partial T)_{av}$ on ΔF for real systems.

From Eq. [15] it follows that the derivative $P = (\partial\Delta F/\partial T)_{av}$, in a region where the Kelvin equation is valid for capillary condensation, should be proportional to ΔF . Figure 4a exhibits the dependence of P on ΔF plotted from the desorption branch of the isotherm for the case of adsorption of benzene on Fe_2O_3 -gel according to reference 13. In the temperature interval studied (40° – 60°C .) the value of σv for benzene decreases linearly with T and K being equal to $d \ln \sigma v / dT \approx -0.0041 \text{ deg}^{-1}$. The straight line 1 in Fig. 4a is drawn at a theoretical slope equal to K . It is evident from the figure that as ΔF grows, the experimental values of the derivative P first fall on line 1, and then, in the vicinity of point K sharply deviate from this line upwards and pass into the region of positive values. In the same Fig 4a values of r , calculated from Eq. [10], are also plotted along the axis ΔF . The point K lies approximately at 16Å. and defines the lower limit of the values of r below which the Kelvin equation evidently is invalid. Thus, the curve of Fig. 4 is especially remarkable in that it makes possible purely thermodynamical determination of the lower limit r_K of the applicability of the Kelvin equation.

When the experimental data obtained from the adsorption branch of the isotherm are plotted in coordinates $\Delta F, P$, the slope of the linear part of the curve is smaller in its absolute value than the theoretical value of K . The possible cause may lie in simultaneous multilayer adsorption and capillary condensation. The superposition of these phenomena may lead to a decrease in the absolute value of ΔS and, hence, P .

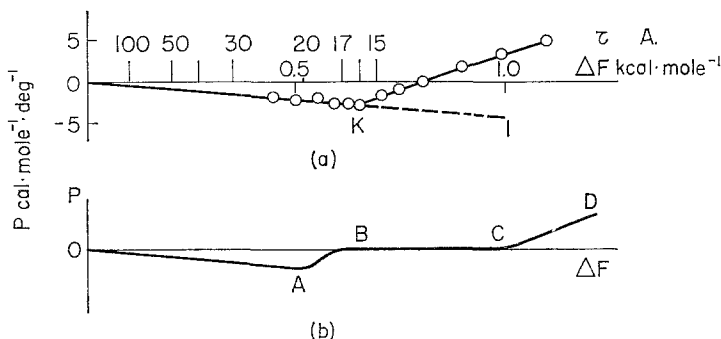


FIG. 4. Dependence of derivative P on ΔF .

Figure 4b displays schematically the trend of the curve $P = f(\Delta F)$ for a more general case of simultaneous existence of the region of temperature invariance and the region of capillary condensation on the isotherm of adsorption; this is observed, for instance, on active carbons with a developed intermediate porosity. In this case, as ΔF grows, the first to appear is the linear interval OA and then, in the region of temperature invariance, the curve should coincide with the abscissa within the section BC and, further on, passing over to small fillings, rise into the region of positive values of P along CD .

If the slope K of the approximately linear portion OA is small, in this case we may expect a satisfactory fulfillment of condition [1] throughout the entire region $OABC$. The value of K is related to the critical temperature T_c of the adsorbate. Indeed, if the Ramsay-Shields equation

$$\sigma v^{2/3} = C(T_c - T - 6), \quad [20]$$

where C is a constant, is valid for a liquid adsorbate, then

$$K = -\frac{1}{T_c - T - 6} + \frac{1}{3}\alpha \approx -\frac{1}{T_c} \frac{1}{1 - \theta}, \quad [21]$$

where θ is reduced temperature. Consequently, at equal values of θ , the area of feasibility of the temperature-invariance condition will be wider for substances with higher critical temperatures T_c .

The region AB in Fig. 4b corresponds to transition to very small values $r < r_K$ for which the Kelvin equation becomes invalid, i.e., to micropores. It could be expected that in this region the adsorption phase compressed in fine pores by the action of the adsorption field will 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 an excess according to Gibbs (even at those values of adsorption which allow us to consider the adsorption phase as condensed), does not vanish at the critical temperature T_c of a bulk liquid phase (14, 15), but exists at $T > T_c$ and, therefore, the difference between the gaseous and condensed adsorption phases does not disappear at $T = T_c$. For this reason we may expect that at very small r 's the absolute value of $\gamma = d \ln \sigma / dT$ will decrease with r , whereas α seems to be practically independent of r or depends on it very slightly. This suggests that 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 condition [1]. If the total volume of pores of such radii (i.e., the micropore volume) is large, the isotherm of adsorption should exhibit a protracted region characterized by the value $K \approx 0$, i.e., a region of temperature invariance. This does not mean, however, that the presence of a region in which $P = 0$ in Fig. 4b necessarily points to the existence of micropores. In certain cases temperature invariance may be observed also

in the absence of micropores. Thus, for example, at small values of K the region of capillary condensation may be practically indistinguishable from the region of temperature invariance. The relative extent of the region OA and OB in Fig. 4b is probably determined by the structure peculiarities of the porous adsorbent.

As a result of analysis of extensive experimental data on adsorption of the vapors of various substances on active carbons, the following equation of a characteristic curve (16) was suggested and substantiated theoretically (17):

$$aw = W_0 e^{-D(\Delta F)^2} = W_0 \exp \left(-\frac{BT^2}{\beta^2} \log^2 \frac{p_s}{p} \right), \quad [22]$$

where $W_0 = a_s v$ is a constant representing the volume of the adsorption space, i.e., the micropore volume; B is a constant independent of temperature and representing the basic characteristic of the porous structure of the adsorbent; β is the affinity coefficient of the characteristic curve $\Delta F = \beta f(aw)$ for the substance under investigation when for a standard substance (usually benzene or nitrogen) $\beta = 1$. It was found experimentally that the coefficient $\beta = (\Delta F_1/\Delta F_2)_{aw}$ remains practically constant for a given pair of substances throughout the entire region of temperature invariance when the value of aw remains unchanged, and in most cases it can be defined as a ratio of the molar volumes v_1 and v_2 or, more precisely, as a ratio of the parachors ϕ_1 and ϕ_2 of the two substances. It is noteworthy that the choice of parachors is more logical than the choice of molar volumes, since only a temperature-independent quantity may serve as the coefficient of affinity of two temperature-invariant curves.

From the characteristic curve Eq. [22] follows the equation of the isotherm of adsorption of vapors on microporous adsorbents (16).

$$a = (W_0/v) \exp (-BT^2\beta^{-2} \log^2 p_s/p). \quad [23]$$

The constant W_0 and B of this equation, which characterize the properties of the adsorbent, can be determined, for instance, from one isotherm of adsorption of a standard substance by plotting the experimental data in the coordinates $\log aw$, $(\Delta F)^2$ or $\log aw$, $(T \log p_s/p)^2$ corresponding to the linear form of the isotherm equation [23].

$$\log aw = \log W_0 - (B/2.30\beta^2)(T \log p_s/p)^2. \quad [24]$$

As a good approximation, the value of v in Eqs. [23] and [24] can be taken to equal the value of a molar volume of a bulk liquid² at temperatures

² As values of W_0 calculated from experiments with different adsorbates are constant for a given adsorbent, it follows that molar volumes of adsorbed substances are proportional to their values for bulk liquids, the proportionality constant being equal for all adsorbates and probably close to unity. For the theory in question, however, the numerical value of this factor is immaterial.

widely differing from T_c . In view of the fact that at higher temperatures the compressibility of the adsorbed substance in the adsorption field should be taken into account, it is necessary to introduce a corrected value $v^* < v$. Two different ways of introducing suitable corrections, which lead to practically identical results, are presented in references 15 and 18.

The two-constant equation [23] gives a fairly accurate quantitative description of adsorption of many classes of substances on microporous adsorbents; in order to calculate the isotherms of adsorption for these substances one should know only the two constants W_0 and B , determined from one isotherm of adsorption of a standard substance and serving as a very concise description of the sorption properties of the adsorbent, and the tabulated values of the parachor as well as the molar volume and pressure of the saturated vapor of the adsorbate. This equation describes especially well adsorption for systems in which dispersion forces play a dominant part in adsorption interactions. It can be applied somewhat less effectively in cases where the role of electrostatic interactions is great. Beyond the region of temperature invariance, i.e., at small fillings of the adsorption volume, or, more precisely, at $\Delta S > 0$, as well as in the region of capillary condensation, this equation cannot yield a correct temperature dependence of adsorption.

If, in a particular case, the characteristic curve in the region of temperature invariance is described by Eq. [22] or, in other words, the linear dependence of $\log av$ on $(T \log p_s/p)^2$ is fulfilled in the coordinates of Eq. [24], then, substituting into Eqs. [17] and [18] the values of the derivative $(\partial \Delta F / \partial \ln a)_T$ calculated from Eq. [23], we obtain (2) the following expressions for differential entropy and differential molar heat of adsorption:

$$\Delta S = -\frac{2.30\alpha\beta R}{2B^{1/2}} \left(\ln \frac{W_0}{av} \right)^{-1/2}; \quad [25]$$

$$Q = \lambda + \frac{2.30\beta R}{B^{1/2}} \left[\left(\ln \frac{W_0}{av} \right)^{1/2} + \frac{\alpha T}{2} \left(\ln \frac{W_0}{av} \right)^{-1/2} \right]. \quad [26]$$

Values of Q calculated from Eq. [26] and determined experimentally for a number of systems studied are, as a rule, in good agreement. By way of illustration, Fig. 5 shows Q vs. a curves for benzene on active carbons obtained by E. F. Polstyanov (19). The upper curve demonstrates the best agreement of the values of Q found from Eq. [26] and from isosteres, and the lower shows the worst agreement of these values, which even in this case do not diverge by more than 5%. Note that for calculating ΔS and Q from these equations it will suffice to know the adsorbent characteristics W_0 and B and the adsorbate characteristics α , β , v , and λ . It should be particularly emphasized that such calculations are meaningful only in the region of applicability of Eq. [23], which may be narrower than the region of temperature invariance.

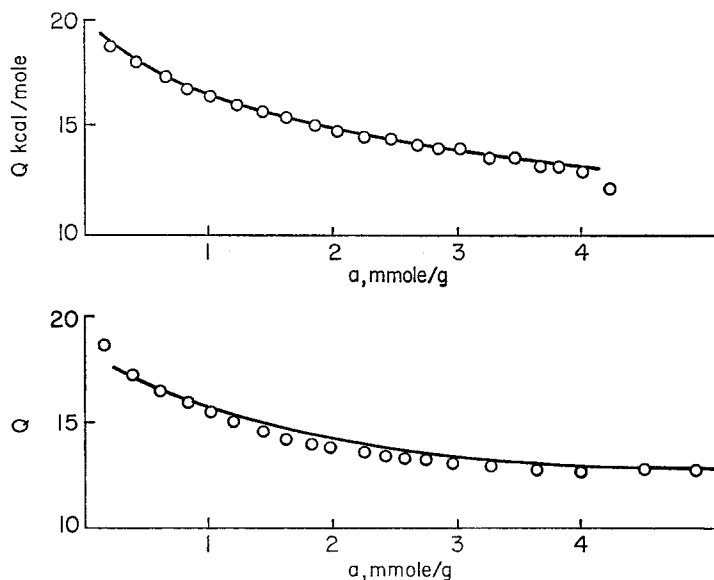


FIG. 5. Relationship between differential heat of adsorption Q of benzene on different active carbons and the value of adsorption a . The solid curves have been calculated by Eq. [26]; \odot —found from the slope of isosteres of adsorption.

In the general case, it would be entirely erroneous to think that in the whole range of applicability of condition [1] a characteristic curve must necessarily be described by Eq. [22], and a number of examples could be quoted, especially in adsorption on zeolites (20), where the region of temperature invariance proves to be wider than the region within which the linear dependence required by Eq. [24] is fulfilled. At the same time, at some single temperature this linear dependence may be fulfilled in a wider interval of adsorption values than the region of temperature invariance. In full agreement with experiment (3) this becomes particularly evident from Fig 3c. Among the family of curves diverging above the region of invariance AC , one can be formally described by Eq. [24] in a wider interval than AC . In this case, however, other isotherms of adsorption will inevitably deviate from linear dependence upon leaving the region AC . It follows from the foregoing that the length of the linear region or the deviation from linearity in the coordinates $\log aw$, $(\Delta F)^2$ for a single isotherm in the general case does not permit judging the length of the region of temperature invariance.

In conclusion we should like to note that Eq. [23] can be generalized (21) to the case of adsorption of a binary mixture of vapors on microporous adsorbents:

$$a_1 + a_2 = \frac{W_0}{N_1 \bar{v}_1 + N_2 \bar{v}_2} \exp \left[-\frac{BT^2}{(N_1 \bar{\beta}_1 + N_2 \bar{\beta}_2)^2} \log^2 \frac{p_{s12}}{p_{12}} \right], \quad [27]$$

where W_0 and B have the same meaning and the same numerical values as in Eq. [23], N_1 and N_2 are molar fractions of the components in the adsorption phase, \bar{v} and $\bar{\beta}$ are the respective partial molar values, $p_{12} = p_1 + p_2$ is the sum of the partial pressures of the components, and p_{s12} is the pressure of saturated vapor over the bulk solution of both components, which has the same composition as that of the equilibrium vapor over the adsorbent. Equation [27] supplies a fair description of experimental data on adsorption of vapor mixtures on microporous adsorbents (21).

It would be wrong to think that the theory of physical adsorption on 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. Despite this, however, it is our opinion that the theory presented here stands out among the majority of the theories of adsorption published so far in the literature in that it gives the temperature dependence of adsorption in explicit terms and makes it possible to calculate from the adsorbent constants W_0 and B and the adsorbate constants v , α , Φ , and p_s isotherms of adsorption within a wide temperature interval, as well as the basic thermodynamic characteristics of adsorption equilibrium, ΔS and Q , for a large number of substances on the important microporous adsorbents, subject to the above-mentioned limitations. Thus, within the indicated framework, this theory solves the basic problem facing the theory of physical adsorption, i.e., quantitative description and the possibility of calculation of the parameters of the adsorption equilibrium of various substances on real microporous adsorbents. To the best of our knowledge none of the known theories of physical adsorption solves this problem so comprehensively. Nevertheless, we clearly realize that the improvement and development of the concepts presented here will require further theoretical and experimental research.

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