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Physical Adsorption on Non-Uniform Surfaces

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Analysis of adsorption on a uniform surface using the quasi-chemical theory of interaction shows that the hypotheses of the BET theory lead to substantially no adsorption beyond the first layer if $E_2 = E_L$, and stepwise isotherms if $E_1 > E_2 > E_3 > \cdots > E_L$. For the monolayer adsorption of gases on silver, platinum, and steel, the heterogeneous nature of the adsorbing surface is clearly indicated. Cooperative adsorption on the non-uniform surface is treated, and the cooperative analog of the Freundlich equation derived. The typical multi-layer isotherm is shown to be composed of three regions: non-cooperative adsorption on a strongly heterogeneous surface; cooperative adsorption on a still heterogeneous surface; and cooperative multi-layer adsorption induced by small van der Waals perturbations some distance from the surface.

The isotherm $p/p_0 = \exp\{-a/\theta^r\}$ is derived and shown to be a good representation of adsorption data that conform to the BET Type I, II, or III shapes.

THE theory of physical adsorption has been greatly advanced by the idea that molecules of a vapor can be adsorbed to a depth of many monolayers. The development of the theory of multilayer adsorption is largely the work of Brunauer, Emmett, and Teller (BET).[1] The original theory has been the subject of many criticisms and refinements,[2] but the picture that the adsorbed layer is many molecules thick near the condensation pressure of the bulk liquid has not been invalidated. In other respects, however, it appears that a more refined treatment of adsorption or a uniform surface destroys rather than corrects the BET theory.

In what follows the notation of Brunauer[1] will be used.

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[1] S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, New Jersey, 1943).
[2] T. L. Hill, J. Chem. Phys. 14, 263, 441 (1946); 15, 767 (1947); H. M. Cassel, J. Phys. Chem. 48, 195 (1944).

I. CRITICISM OF THE BET THEORY

The original BET equation gives the coverage, measured in monolayers, as

$$\theta = v/v_m$$
$$= (p/p_0)/(1 - p/p_0)\{1/c + (c - 1/c)p/p_0\}. \quad (1)$$

In order to criticize the BET theory only the case $c = 1$ need be considered. For $c \to \infty$, $\theta = \theta_{c=1} + 1$, and the argument will be generalized to intermediate values of c.

$$\theta_{c=1} = (p/p_0)/(1 - p/p_0). \quad (2)$$

This result is based on the quite untenable hypothesis that an isolated adsorbed molecule can adsorb a second molecule on top, yielding the full energy of liquefaction, and that in turn the second molecule can adsorb a third, and so on. However, it is more nearly true to assume that for hexagonal packing at least a triangular array of adsorbed molecules would be required to

adsorb another with the release of energy approaching the heat of liquefaction.

Consider the point $p/p_0 = 1/2$. Here the BET coverage in the first layer, θ_1, is $1/2$. The fraction of sites in the second layer with filled triangular array beneath is $(1/2)^3$. If these sites are filled to the BET amount then $\theta_2 = (1/2)^4$. The fraction of sites in the third layer with a filled triangular array beneath is then $(1/2)^{12}$! It is thus apparent that the third layer is effectively empty. θ_2 is then reduced to the Langmuir adsorption $(1/2)^3 \times 1/3$ because it is not protected from evaporation by the BET coverage above. Therefore, θ_1 itself becomes almost unprotected and assumes the Langmuir coverage $1/3$. This decrease further reduces θ_2 to the negligible value of $(1/3)^4$. Thus, at $p/p_0 = 1/2$ and below, only a monolayer exists, and the coverage is given by the Langmuir expression

$$\theta = (p/p_0)/(1 + p/p_0). \tag{3}$$

It is apparent that unless θ_1 rises above *ca.* $1/3$, the second layer is not formed in appreciable quantity. Keeping this fact in mind, attention may now be focused on the artificial problem where the second layer is prohibited from forming

FIG. 1. The adsorption of nitrogen on platinum.

by a capillary wall. This problem is equivalent to the problem without such a wall as long as $\theta_1 < 1/3$. Equation (3) is the solution of this problem for the non-cooperative case.

The refined (quasi-chemical) treatment of Fowler and Guggenheim[3] for localized monolayers will be used to obtain the solution for the cooperative case. Employing their notation the expression for pressure is (Eq. (1012.9))

$$p(\theta) = p^0(\theta/1-\theta)[(2-2\theta)/(\beta+1-2\theta)]^z,$$

where

$$\beta = [1 - 4\theta(1-\theta)(1 - \exp\{-2w/zkT\})]^{1/2}.$$

(The constant p^0 is a reference pressure, not to be confused with p_0, the condensation pressure of the bulk liquid.)

In the case of attractive interaction (negative w) two-dimensional condensation begins at a θ_{conds} which is the smallest root of $p(\theta) = p(1/2)$. It will emerge that the square of this small θ can be neglected. Making this approximation, one finds

$$\theta_{conds} \fallingdotseq \exp\{w/kT\}. \tag{4}$$

Because adsorption takes place on a liquid-like surface, the molal free energy of the completed film equals that of the liquid:

$$\log p_0 = \int_0^1 \log p(\theta) d\theta.$$

Fowler and Guggenheim show that $\log p(\theta)/p(1/2)$ is an odd function of $\theta - 1/2$. Thus

$$\int_0^1 \log p(\theta) d\theta = \log p(1/2),$$

$$p_0 = p(1/2),$$

and therefore two-dimensional condensation begins when $p/p_0 = 1$, in harmony with the assumption of a liquid-like surface. Below condensation

$$\theta = (p/p_0) \exp\{w/kT\}.$$

Hexagonal packing will be assumed in order to find the value of w. There are six neighbors in a two-dimensional film and twelve in the liquid. Therefore, the energy of interaction in the film is

[3] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Teddington, England, 1939).
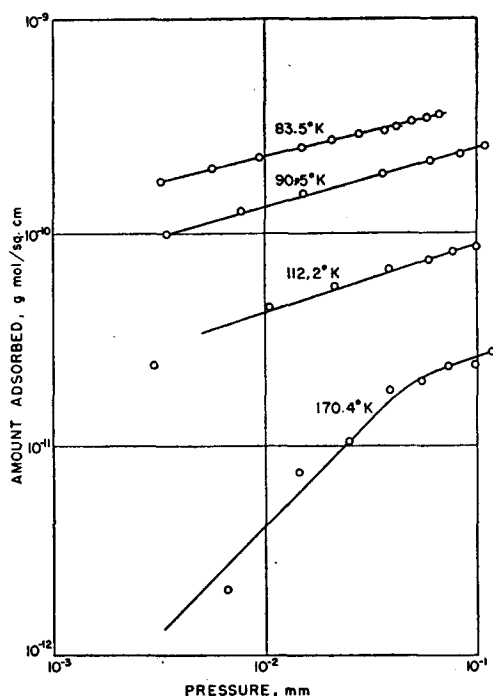
approximately $1/2E_L$. The number of pair inter-actions per molecule is $Z/2$. The energy per pair is $2w/Z$. Therefore, $(2w/Z)(Z/2) = -E_L/2$ and $-w = E_L/2$.

For the adsorption of nitrogen at 77°K, $E_L = 1330$ cal./mole. Therefore, θ_{conds} (from Eq. (4)) $= 0.015$. Trouton's rule indicates that a similar or smaller value is to be expected for most liquids at or below the boiling point. Thus, below $p/p_0 = 1$, θ remains below 2 percent coverage, justifying the assumptions that $\theta < 1/3$ and that θ^2 can be neglected. Therefore, it appears that instead of observing the BET adsorption indicated by Eq. (2) or even the Langmuir adsorption of Eq. (3), a surface with the above properties is incapable of condensing further layers at any pressure below saturation. One must thus draw the conclusion that on the basis of the BET hypotheses the adsorption for any value of c is actually confined to the amount accommodated in the first layer. Adsorption in the second layer becomes the negligible quantity $\theta_1{}^3 p/p_0 \exp\{w/kT\}$, smaller by a factor $\theta_1{}^3$ than the adsorption on a liquid-like surface.

Discarding the hypothesis that $E_2 = E_L$ is not sufficient to restore the BET theory. The treatment of cooperative adsorption can be extended to include surfaces whose adsorption energy is ΔE greater than that of the liquid. Two-dimensional condensation is found to begin at $\theta = \exp\{w/kT\}$ and

$$p/p_0 = \exp\{-\Delta E/RT\}. \tag{5}$$

It is reasonable to assume that w is unchanged by a change in the attraction between the surface and the adsorbed molecule. Thus, the value of θ at which condensation begins is unchanged. A multilayer isotherm based on the hypothesis $E_1 > E_2 > \cdots > E_L$ must lead to an isotherm composed of a series of steps.

When mobile adsorption is assumed, the results presented above are not altered significantly. If $\log p(\theta)/p(1/2)$ is an odd function of $\theta - 1/2$ they are unchanged.

II. MONOLAYER ISOTHERMS

When adsorption data are fitted to the Langmuir equation, it is often found that the apparent maxima of adsorption are a function of temperature. F. J. Wilkins studied the adsorption
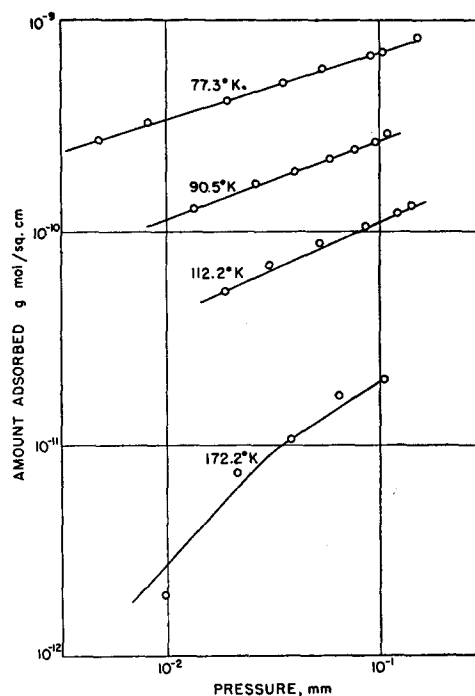

FIG. 2. The adsorption of argon on platinum.

of nitrogen, argon, and oxygen at temperatures from 77.3°K to 194.5°K.[4]

The adsorption isotherms could be fitted by the Langmuir equation in most cases; but V_{max} varied 10–100 times with temperature. These data form an extreme case of the violation of the Langmuir postulate that the number of sites is constant. Wilkins' theoretical treatment directed at removing this limitation is not valid. He assumes that only a certain fraction of the surface area is available for adsorption, and that the size of this "island" varies continuously with temperature. Clearly, such an assumption presupposes a continuously non-uniform surface.

Contrary to this, Wilkins states (p. 502), "It has been tacitly assumed that the adsorption potential is constant throughout the adsorption volume." This inconsistent assumption allows him to develop the Langmuir equation within the "island."

It should be pointed out in passing that the correction applied to the Clausius-Clapeyron equation proposed by Wilkins, and discussed by

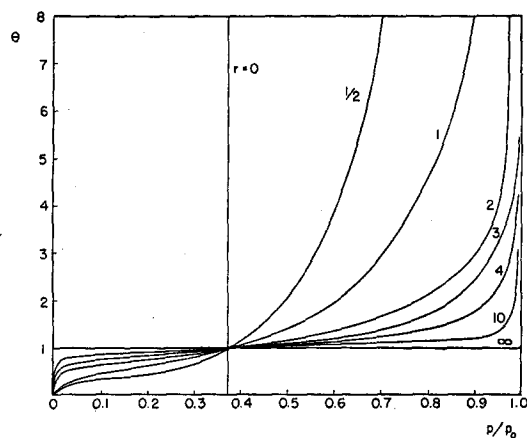[4] F. J. Wilkins, Proc. Roy. Soc. A164, 496 (1938); ibid., 510.

FIG. 3. The isotherm $p/p_0 = \exp\{-1/\theta^r\}$ plotted for various values of r.

Armbruster and Austin[5] is erroneous. Corrected for gas imperfections, the equation is thermodynamically sound, as may be easily proven by the application of Gibbsian method.

The rejection of this equation apparently originated in the observation of McBain[6] that because of the varying maxima of adsorption obtained with the Langmuir isotherm, application of the equation was impossible; the answer is that the maxima are only apparent.

Halsey and Taylor have shown that the adsorption of hydrogen on tungsten is explained by a non-uniform surface,[7] characterized by an exponential distribution of adsorption energies. Such a distribution leads to an isotherm identical with the classical Freundlich isotherm. The widespread applicability of the Freundlich isotherm, and its origin in a distribution of adsorption energies are very significant when considered together. Although Zeldowitsh[8] derived the isotherm by an approximate process many years ago, textbooks dismiss it as the middle region of the Langmuir isotherm. Such an explanation can only apply over a limited pressure range while the Freundlich isotherm is often valid over many cycles of $\log p$.

It should be noted that strong repulsive inter-

actions, dismissed on quantitative ground elsewhere,[7] do not lead naturally to the Freundlich law, but to an isotherm of the type $\log p \approx a\theta + b$. In addition, when adsorption takes place on a strongly non-uniform surface, it is quite proper to assume non-interactive adsorption when cooperation would take place on a uniform surface. This situation exists because it is quite reasonable to expect that the sites are so dispersed that the number of neighbors of a given energy is nearly zero. Finally, it will appear later that a distinction between cooperative and non-cooperative adsorption is not possible when the surface is very non-uniform.

Considering the success of the Freundlich plot in the case of hydrogen on tungsten, it is of interest to examine Wilkins' data on platinum in that form. Figures 1 and 2 show the data for nitrogen and argon, respectively. The general similarity to the Frankenburg data for tungsten is immediately apparent; it is as if a section, both with respect to temperature and pressure, were selected from Frankenburg's data.

The general similarity extends to the region of sparse coverage, where the slope on double logarithmic coordinates approaches unity, and the Langmuir equation becomes applicable. To infer from this that the Langmuir equation can also be applied to the high coverage isotherms is in error, because these Langmuir sites represent at most one percent of the total available sites.

When the data are plotted in this manner the achievement of the adsorption "maximum" at the higher temperatures clearly becomes illusory. An increase in pressure must ultimately lead to the total coverage of the surface, but for higher temperatures the pressures may have to become prohibitively large.

M. H. Armbruster's data[9] on the adsorption of gases on silver are similar to those of Wilkins, although considerably less extensive. The isotherms, over the limited range investigated, again conform to the Langmuir equation. The usual discrepancies are noted, however. Saturation maxima are a function of temperature. In fact, only a small fraction of the geometrical surface is covered. Only in the case of oxygen, where chemisorption is involved, does the fraction of

[5] M. H. Armbruster and J. B. Austin, J. Am. Chem. Soc. 66, 159 (1944).

[6] J. W. McBain, Sorption of Gases and Vapours (Routledge, London, 1932).

[7] G. Halsey and H. S. Taylor, J. Chem. Phys. 15, 624 (1947); see also R. Sips, J. Chem. Phys. 16, 490 (1948).

[8] J. Zeldowitsh, Acta Physicochimica U.R.S.S. 1, 961 (1934).

[9] M. H. Armbruster, J. Am. Chem. Soc. 64, 2545 (1942).

the geometrical surface covered approach unity. A non-uniform surface is thus indicated.

Armbruster and Austin[5] determined a large number of isotherms for gases on steel. The authors apply the methods of Wilkins to their data. It is pertinent to observe that they find: "The value of v_s [coverage at saturation] increases markedly with decreasing temperature, as is common in systems of this type." The non-uniform surface is again indicated.

Both Armbruster and Austin and Wilkins calculate the adsorption maxima, even when these are not reached, by using the Langmuir equation. It appears that the process might be deceptive. In attempting to discover a suitable isotherm for their data Armbruster and Austin remark "it [the Freundlich isotherm] fits very well over the low pressure range. . . . The equation fails, as it must as the surface approaches saturation." The slight bending over of the isotherm on the Freundlich plot, which the authors take to mean saturation cannot be considered conclusive. In many of the isotherms investigated the geometrical surface of the steel is not yet covered.

III. COOPERATIVE ADSORPTION AND THE FORMATION OF MULTILAYERS

Because on many surfaces the sites of low energy are much more numerous, the importance of cooperative adsorption increases with the progress of adsorption from the high energy sites to those of lower energy. Eventually the number of neighbors being adsorbed simultaneously may become large enough to cause cooperative condensation. If sites of nearly equal energies are localized into patches, this cooperation is facilitated because the number of effective neighbors is increased. Molecules adsorbed side by side but at differing pressures do not constitute neighbors in the cooperative sense because cooperation implies that the molecules influence one another's adsorption. A molecule adsorbed at a high pressure may contribute its energy to improve an adjacent site of lower energy; but, in doing so, it does not influence its own adsorption; it becomes evident that a knowledge of molecular topography is necessary to predict what kind of adsorption will take place.

If the surface is characterized by a distribution

function of cooperative adsorption energies $N_{\Delta E}$, the pressure at which the sites with energy ΔE are filled is given by Eq. (5) and the expression for coverage is

$$\theta = \int_{-RT \log p/p_0}^{\infty} N_{\Delta E} d\Delta E.$$

If $N_{\Delta E}$ has the exponential form $c \exp\{-\Delta E/\Delta E_m\}$,

$$\theta = c'(p/p_0)^{RT/\Delta E_m}, \qquad (7)$$

analogous to the Freundlich isotherm, which can be derived from the same distribution when interactions are not allowed. The only difference is that in the non-cooperative case the exponent must be less than unity because of the convergence condition $\Delta E_m/RT > 1$. If this condition is met, the two modes of adsorption are indistinguishable, while if $\Delta E_m/RT < 1$, the second derivative is positive, a phenomenon possible only with cooperative effects.
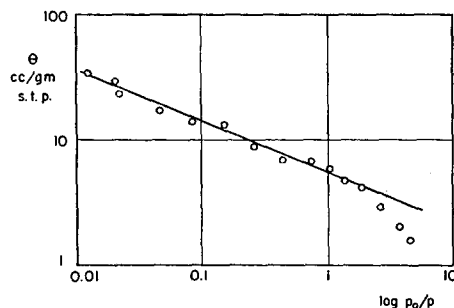

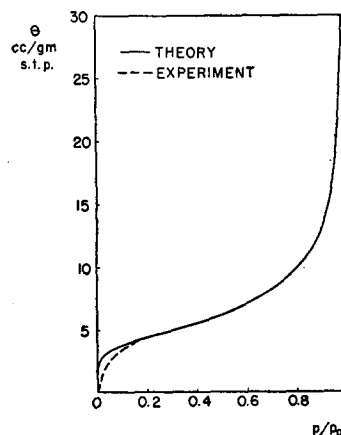FIG. 4. Adsorption of water on anatase at 25°C plotted according to Eq. (11).

FIG. 5. The isotherm for water on anatase fitted to Eq. (10) with $r = 2.5$.

It is interesting to note that not only the Langmuir and the step-condensation isotherms lead to the Freundlich law when an exponential distribution is used. The isotherm $p(\theta)=\varphi(\theta)\exp\{-\Delta E/RT\}$ where $\varphi(\theta)$ is any function of θ independent of ΔE will lead to the same isotherm.

Owing to the neglect of the sites provided by the previously adsorbed gas, the generalized Freundlich isotherm does not approach $\theta=\infty$ at $p/p_0=1$. A modified treatment can provide for this situation. At some distance, x, from the surface, assume that the van der Waals energy ΔE falls off according to a law $E=\chi'(x)$. Now the volume adsorbed is proportional to the depth of the layer, so the energy can be written $E=\chi(\theta)$. Using Eq. (4), the isotherm becomes

$$p/p_0=\exp\{-\chi(\theta)/RT\}. \tag{8}$$

For the specific law $\Delta E=a\theta^{-r}$ the isotherm obtained is

$$p/p_0=\exp\{-a/RT\theta^r\}. \tag{9}$$

This equation not only satisfies the above requirements but is of general utility and it will be discussed in detail below.

The typical experimental isotherm can be divided into three parts. The first part consists of adsorption without cooperation on the more active parts of the surface, described in Part II. Secondly, a cooperative adsorption takes place on the still heterogeneous surface resulting from the initial adsorption. A certain amount of this subsequent adsorption takes place on bare surface, the remainder on the surface of the previously adsorbed gas, under the influence of transmitted van der Waals forces. In general, enough molecules are being adsorbed at once when $\Delta E\sim RT$ (or $p/p_0=1/e$) to allow cooperation. A clear
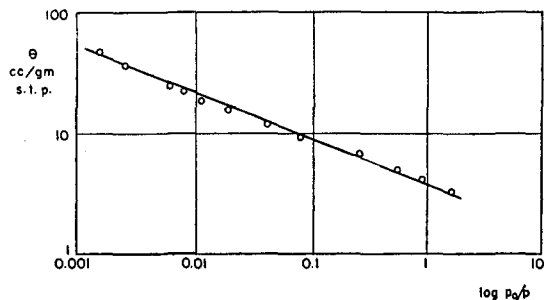
manifestation of cooperation is a positive $d^2\theta/dp^2$. In the pressure region near condensation, the third part of the isotherm begins—a cooperative multilayer condensation under the influence of the weak van der Waals field transmitted from the surface. The intense forces acting at large distances required by the old potential theory are not needed, because only a small fraction of RT causes two-dimensional condensation at pressures near $p/p_0=1$, when the perturbation is added to the E_L provided by cooperation.

The three regions into which isotherms can be divided are not necessarily all manifest in a given isotherm; in the BET "type III" isotherm, where $d^2\theta/dp^2$ is always positive, the first region is missing. In Type I only the first portion is apparent. W. J. C. Orr's[10] adsorption isotherms for non-polar gases on KCl show the three regions nicely separated. Thus argon at 79.35°K is adsorbed without cooperation on a heterogeneous surface until pressure reaches 1.5 cm. Here an inflection point is reached, and cooperative adsorption begins. That this adsorption takes place on a limited surface is shown by its reaching an apparent saturation. This is followed by a second inflection point leading to multilayers and condensation. Nitrogen and oxygen behave similarly.

The calculated heat curves confirm this interpretation. The heat declines during the non-cooperative adsorption; it passes through a minimum and begins to increase as cooperative adsorption takes place. It reaches a maximum and declines as the monolayers add out into space.

It is to be emphasized that the explanation of any of the experimental isotherms in the BET classification (Types I to V) invokes the presence of a non-uniform surface. Paradoxically enough, the obeying of the Langmuir isotherm is frequently a positive indication that the surface is non-uniform enough to make cooperative adsorption impossible. It is for this reason that the Langmuir isotherm is most successful when it treats adsorption (most often chemisorption) where only a small fraction of the surface is available for adsorption.

IV. A WORKING ISOTHERM

It is apparent that an isotherm equation embracing all the possibilities discussed above would

FIG. 6. Adsorption of nitrogen on anatase at $-197°C$ fitted from $p/p_0=0.0026$ to 0.9936 by $r=2.67$.

[10] W. J. C. Orr, Proc. Roy. Soc. 173, 349 (1939).

be too complex to have utility. On the other hand, many of the data of adsorption have a simplicity that allows them to be fitted to an expression with two parameters.

Equation (9) was developed to provide an expression for condensation of multilayers at a relatively large distance from the surface. Strictly speaking, close to the surface it should be replaced by a series of steps. However, the non-uniform nature of the surface smooths out these steps and makes the equation approximately valid beyond the first layer. At a coverage less than one monolayer, the concept of the field decaying with distance is replaced by the distribution function of adsorption energy that leads to an equivalent isotherm. This distribution corresponds to a strongly heterogeneous surface where the cooperative adsorption implied in the derivation is not distinguishable from non-cooperative adsorption.

This situation arises because, in general, when a distribution is wide enough, the functional form of the isotherm for adsorption at a given energy does not influence the form of the isotherm integrated over all values of the adsorption energy.

A considerable adsorption takes place near $p/p_0 = 0$, giving rise to an "initial" adsorption characteristic of the "Type II" isotherm. If adsorption is measured in multiples of the adsorption at $p/p_0 = 1/e$ the isotherm takes the form

$$p/p_0 = \exp\{-\theta^{-r}\}, \qquad (10)$$

with an inflection at $p/p_0 = \exp\{-r+1/r\}$ and $\theta = (r/1+r)^{1/r}$. Equation (10) is plotted in Fig. 3 for various values of r. As r decreases, the point of inflection moves toward the origin, and the isotherms assume the "Type III" form. As r increases, they take on a "Type I" shape.

Using an empirical equation of state for a condensed monolayer, Harkins and Jura[11] have derived the isotherm

$$\log p/p_0 = A/v_0^2 - B/v^2,$$

where v is the volume of gas adsorbed at p, and v_0 the volume at p_0. In the absence of capillaries, $v_0 = \infty$, and the equation becomes $p/p_0 = \exp\{-B/V^2\}$. This is a special case of Eq. (10), with $r = 2$. Hence, the Harkins-Jura equation of state corresponds to a model in which the attraction of the interface falls off with the second power of the distance. When transformed by the Gibbs adsorption formula, Eq. (10) yields the generalized equation of state

$$\pi = a - b\sigma^{r-1}.$$

For purposes of curve fitting, Eq. (10) is put in the form

$$\log\log(p_0/p) = r\log\theta, \qquad (11)$$

and the constant r evaluated from the slope. In Fig. 4 the data of Harkins and Jura for the adsorption of water on anatase are so plotted. Equation (11) is valid between $p/p_0 = 0.2$ and 0.98. The fitted isotherm (Fig. 5) shows the extent of the deviation, with $r = 2.5$. Figure 6 shows the data for nitrogen on anatase plotted according to Eq. (11), with $r = 2.67$. Agreement extends from $p/p_0 = 0.0026$ to 0.9936.

The data of Boyd and Livingston[12] show a wide variation of the constant r in different isotherms. Estimating from their published curves, r has a value of about 6 for the adsorption of propyl alcohol on anatase, and at least 15 for the same vapor on $BaSO_4$. On the other hand, for the adsorption of water on graphite r is about unity.

If r is very large, the attraction of the solid for the vapor is very specific and does not extend far from the surface. When r is smaller, the forces are more typically van der Waals and are able to act at a greater distance. The magnitude of r characterizes the type of interaction between a vapor and a solid.

Note added in proof: The BET surface area determination has not been discussed here. Despite the unreality of the isotherm equation, the nitrogen areas seem completely satisfactory; the reasons will be discussed elsewhere.

[11] W. D. Harkins and G. Jura, J. Am. Chem. Soc. 66, 1366 (1944).

[12] G. E. Boyd and H. K. Livingston, J. Am. Chem. Soc. 64, 2383 (1942).