

Statistical Mechanics of Multimolecular Adsorption. III. Introductory Treatment of Horizontal Interactions. Capillary Condensation and Hysteresis^{1 a}

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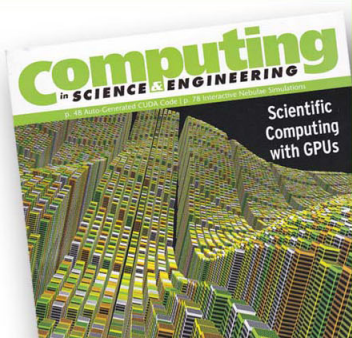
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Statistical Mechanics of Multimolecular Adsorption. III. Introductory Treatment of Horizontal Interactions. Capillary Condensation and Hysteresis^{1a}

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The elementary treatment of interactions and first order phase changes in localized and mobile monolayers is reviewed. Calculations on multimolecular adsorption and capillary condensation, which take into account horizontal interactions in an approximate manner, are presented. Several other topics are discussed briefly, including the quasi-chemical method and reversible hysteresis. It is suggested, on the basis of the capillary condensation calculations, that reversible hysteresis involves the use of metastable portions of the adsorption isotherm. The theory predicts, in agreement with experiment, that the adsorption curve should be below the desorption curve.

I. INTRODUCTION

IT is well known that the Brunauer-Emmett-Teller (BET) theory^{1b} of multimolecular adsorption ignores horizontal interactions between adsorbed molecules. This is clear from the model which may be used in a statistical treatment to obtain the BET equation.^{2,3} On the other hand, interactions between adsorbed molecules in the simpler case of monomolecular adsorption (these are, of course, necessarily horizontal interactions) have been taken into account in earlier work.⁴⁻⁷

In Section II we shall review briefly the elementary treatment of interactions and first order phase changes in monolayers. Then, in Sections III (adsorption on a free surface) and IV (adsorption between parallel walls), we shall discuss multimolecular adsorption, including horizontal interactions. However, these latter remarks will be based on calculations using equations which take the interactions into account in only a very approximate manner. So it will not be possible to come to definite conclusions here, and it would certainly be premature to try to compare the theory with experiment (except qualitatively) at this time.

In Section V we give somewhat more general equations, but calculations based on these equations have not yet been carried out. Several other points, including hysteresis, will also be discussed.

^{1a} Presented at the symposium on gas adsorption of the Division of Colloid Chemistry, Chicago, September 11, 1946.

^{1b} S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).

² T. L. Hill, *J. Chem. Phys.* **14**, 263 (1946).

³ A. B. D. Cassie, *Trans. Faraday Soc.* **41**, 450 (1945).

⁴ H. M. Cassel, *J. Phys. Chem.* **48**, 195 (1944).

⁵ In writing part II of this series, the paper⁴ by Cassel had not come to the writer's attention. In this paper, Cassel obtained Eq. II (59), and essentially also Eq. II (38) by a thermodynamic use of a two-dimensional van der Waals' equation. This method is, however, less general since it does not allow an evaluation of the constant C . The statistical treatment gives C .

⁶ R. H. Fowler, and E. A. Guggenheim, *Statistical*

Thermodynamics (Cambridge University Press, London, 1939), Chapter X.

⁷ T. L. Hill, *J. Chem. Phys.* **14**, 441 (1946).

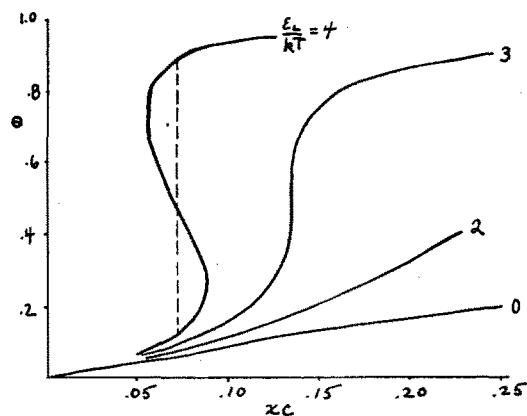


FIG. 1.

II. MONOMOLECULAR ADSORPTION

There are two special cases of particular interest: the adsorbed molecules may be localized at definite sites or they may be mobile, behaving as a two-dimensional gas. Intermediate cases are also possible and the transition may be studied theoretically,⁷ but we shall not discuss this question here. Of the two special cases to be considered, mobile adsorption is probably the most important except at very low temperatures.⁷

Localized Adsorption

The calculations given here for both monomolecular and multimolecular adsorption are for a simple cubic lattice. The calculations for a monolayer are no more difficult for a close packed arrangement, but the equations for multimolecular adsorption do become more complicated (see Section V).

We have to evaluate the potential energy of interaction between the adsorbed molecules somehow. We do this by counting up the number of pairs of nearest neighbor sites occupied by adsorbed molecules. We make the very crude assumption that the available sites on the surface are occupied by adsorbed molecules in a completely random fashion. The next higher approximation would be to use the quasi-chemical equilibrium method.⁶ However, this refinement does not here lead to any new qualitative features but only to quantitative improvements.

On these assumptions, one finds⁶ for the adsorption isotherm (Eq. (1) is a special case of

Eq. (9), to be derived below),

$$xc = \frac{\theta}{1-\theta} \exp\left(-\frac{4}{3} \frac{\epsilon_L}{kT} \theta\right), \quad (1)$$

where θ is the fraction of the available sites occupied, $x = p/p_0$ is the relative pressure, c is the familiar BET constant, and $-\epsilon_L$ is the average potential energy of the molecules in the liquid state (the meaning of ϵ_L is discussed more carefully in Section V). Isotherms calculated from Eq. (1) are shown in Fig. 1. For

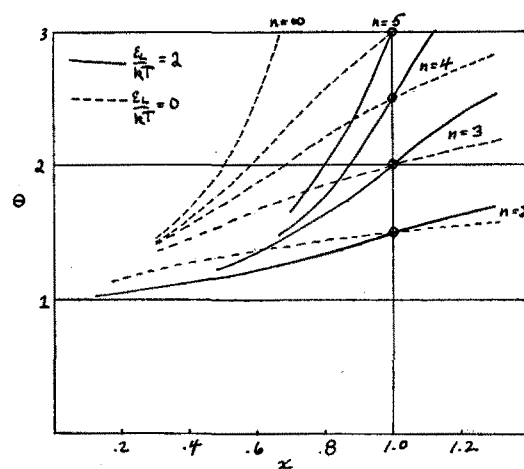


FIG. 2.

sufficiently large values of ϵ_L/kT , a first order phase change is predicted. The critical constants are $\theta_c = \frac{1}{2}$, $T_c = \epsilon_L/3k$ and $x_c c = e^{-2} = 0.1353$. Since c is commonly of the order of 100, this critical behavior is to be expected at low pressures: x of the order of 10^{-3} . The curve for $\epsilon_L/kT = 0$ is the Langmuir isotherm: $xc = \theta/(1-\theta)$.

Mobile Adsorption

We are faced here with the same difficult problem as in three dimensions: what is the equation-of-state of the gas? The reduction from three to two dimensions does not introduce any appreciable simplification. Also, the two-dimensional problem is complicated by the effects of the surface on the molecular interactions. For simplicity, and in the absence of any satisfactory alternative, we assume a two-dimensional van

der Waals' equation:

$$\left(\varphi + \frac{a'N^2}{\alpha^2}\right)(\alpha - Nb') = NkT. \quad (2)$$

In Eq. (2), φ is the two-dimensional (spreading) pressure, α is the area, N the number of molecules adsorbed in the area α , and a' and b' are two-dimensional van der Waals' constants. The adsorption isotherm which can be derived from this equation-of-state^{4,7} is

$$xC = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - \alpha\theta\right), \quad (3)$$

$$\theta = Nb'/a, \quad \alpha = 2a'/b'kT. \quad (4)$$

The constant C is the analogue, for the mobile case, of the BET constant c . It is discussed further in Paper II of this series. The term $\theta/(1-\theta)$ in the exponential is due to repulsions

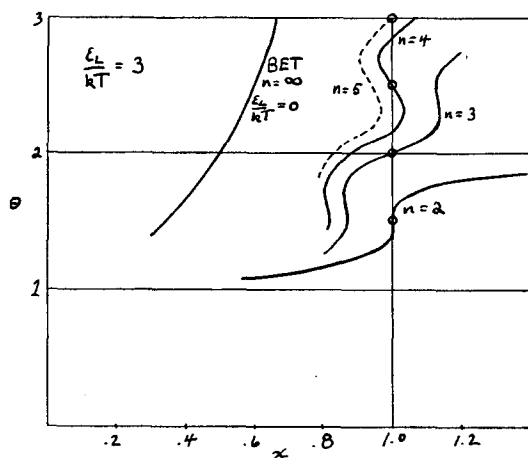


FIG. 3.

(finite volume of spheres) and has no counterpart in Eq. (1). The isotherms calculated from Eq. (3) (these isotherms are given in Fig. 2 of Paper II) exhibit the same general features as seen in Fig. 1 for the localized case. The critical constants are $\theta_c = \frac{1}{3}$, $T_c = 8a'/27b'k$ and $x_c C = 0.0869$. The comparisons between this critical temperature and the three-dimensional critical temperature and between these critical constants and experimental critical constants for *n*-heptane are discussed in some detail in Paper II and will not be repeated here.

III. MULTIMOLECULAR ADSORPTION ON A FREE SURFACE

The model on which the familiar BET equation,

$$\theta = \frac{v}{v_m} = \frac{cx}{(1-x)(1-x+cx)}, \quad (5)$$

(where θ is the ratio of the number of molecules adsorbed per unit area to the number of available sites in the first layer per unit area) is based is the following: the first layer is localized; molecules build up higher layers by adding vertically to molecules already adsorbed; and horizontal interactions between molecules are neglected in all layers. Successive improvements in the BET model would follow from (1) taking into account horizontal interactions, (2) using a lattice more suitable than simple cubic and (3) allowing a more general type of filling in of the lattice.² In this paper we allow for (1) in a very crude way and, in Section V, we introduce other lattices approximately, as suggested by (2). However, all of the preliminary calculations given in this section and in Section IV are based on the simpler equations, to be derived below, for a simple cubic lattice.

The first layer is handled as described in Section II. There are again the two possibilities: the first layer is localized or it is mobile. We assume here that higher layers build up by vertical additions in the simple cubic lattice, each molecule being above a molecule in the layer below (so far, this is just the BET model). If there are X_i molecules per unit surface area in

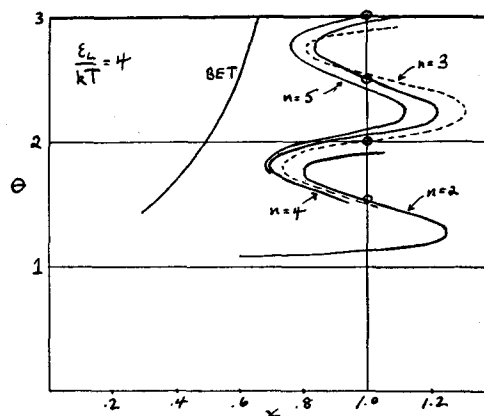


FIG. 4.

the i -th layer, then there are X_i sites available for molecules going into the $(i+1)$ -th layer. Suppose that there are B sites per unit surface area available in the first layer ($B=1/b'$ in the mobile case). For the higher layers we make the same crude approximation, in order to count nearest neighbor pairs, that we made for the first layer in the localized case: we assume that the X_i molecules in the i -th layer are distributed completely at random over the B sites of the i -th layer (not all *available*) and the X_{i+1} molecules of the next higher layer are distributed at random over the X_i available sites and hence at random over all the B sites of the $(i+1)$ -th layer. Consider a lattice site in the i -th layer, with z' nearest neighbor sites *in this layer* ($z'=4$ here). The probability that any site is occupied is X_i/B . Hence, any molecule in this layer has, on the average, $z'X_i/B$ nearest neighbors. So the total number of nearest neighbor pairs in this layer is

$(\frac{1}{2})(X_i)(z'X_i/B) = (\frac{1}{2})(z'X_i^2/B)$. The factor $\frac{1}{2}$ prevents us from counting each pair twice.

One can proceed now to derive directly the equations for $n = \infty$ (n being the number of layers allowed—in imagination—on the free surface) and for either a localized or mobile first layer. However, it proves helpful in the calculations to use the equations for n finite (although the case of physical interest is $n = \infty$), so we shall derive these latter equations (first for the localized case) and let $n \rightarrow \infty$ later.

Suppose that N molecules have been adsorbed in n layers. Then,

$$N = X_1 + X_2 + \cdots + X_n. \quad (6)$$

From Eq. (32) of Paper I (see also Eqs. (19)–(21) in that paper), we have for the partition function (see the discussion of the quasi-chemical equilibrium method in Section V for a more careful treatment),

$$Q = \sum_{X_1} \cdots \sum_{X_{n-1}} \left\{ \frac{[j_s \exp(\epsilon_1/kT)]^{X_1} j_L^{N-X_1} B! \exp(2\epsilon_L \mathfrak{N}/zkT)}{(B-X_1)!(X_1-X_2)! \cdots (X_{n-1}-X_n)! X_n!} \right\}, \quad (7)$$

where X_n is understood to be a function of $N, X_1, X_2, \cdots, X_{n-1}$ as given by Eq. (6), $j_s \exp(\epsilon_1/kT)$ is the partition function⁸ for an isolated molecule on the surface, $j_L \exp(\epsilon_L/kT)$ is the partition function⁸ for a molecule in the liquid state, \mathfrak{N} is the total (average) number of pairs of nearest neighbors (not just horizontal pairs) and is a function of $N, X_1, X_2, \cdots, X_{n-1}$, and, finally, z is the *total* number of nearest neighbors in the lattice (and in the liquid since the lattice is supposed to be liquid-like). $z=6$ for a simple cubic lattice. The BET equation follows² from Eq. (7) if we put $n = \infty$, $\mathfrak{N} = N - X_1$, and $z = 2$ (i.e. ignore the four nearest neighbors in the same layer ($z'=0$), and count only vertical nearest neighbors). In the model we are describing here, $z=6$ ($z'=4$) and

$$\mathfrak{N} = (2X_1^2/B) + (2X_2^2/B) + \cdots + (2X_n^2/B) + N - X_1. \quad (8)$$

⁸ The liquid partition function is discussed further in Section V. $j_s = j_j j_n j_v$ where j is the internal partition function, j_n is the partition function for vibrations normal to the surface (one degree of freedom), and j_v is the partition function for vibrations parallel to the surface (two degrees of freedom). In the mobile case j_v goes over⁷ into the partition function for a molecule in a two-dimensional gas.

$N - X_1$ is the contribution to \mathfrak{N} of vertical pairs of nearest neighbors (as in the BET theory) while the other terms represent, approximately, the number of pairs of horizontal nearest neighbors.

The adsorption isotherm now follows from Eqs. (7) and (8) in a straightforward way already described.² One finds the set of n equations:

$$\begin{aligned} x &= \frac{\theta_1 - \theta_2}{1 - \theta_1} \frac{1}{c} \exp[a(-4\theta_1)] \\ &= \frac{\theta_2 - \theta_3}{\theta_1 - \theta_2} \exp[a(-4\theta_2 + 2)] \\ &\quad \vdots \\ &= \frac{\theta_n}{\theta_{n-1} - \theta_n} \exp[a(-4\theta_n + 2)], \\ \theta &= v/v_m = \theta_1 + \theta_2 + \cdots + \theta_n, \\ \theta_i &= X_i/B, \\ a &= \epsilon_L/3kT. \end{aligned} \quad (9)$$

It is easy to see that, for a mobile first layer, all of these n equations are the same as given here

except the first, which becomes

$$x = \frac{\theta_1 - \theta_2}{1 - \theta_1} \frac{1}{C} \exp\left(\frac{\theta_1}{1 - \theta_1} - \alpha\theta_1\right), \quad (10)$$

$$\alpha = 2a'/b'kT.$$

We are interested in the solution, $\theta(x)$, of Eqs. (9) for $n = \infty$. There does not seem to be any hope of obtaining an explicit expression⁹ for $\theta(x)$ so one must resort to numerical procedures. In principle, the case $n = \infty$ can be solved directly as follows, for given values of x , c and a : guess θ_1 ; using this θ_1 , calculate θ_2 from the first equation; using θ_1 and θ_2 , calculate θ_3 from the second equation; etc. The test of whether θ_1 has been guessed correctly is $\lim_{i \rightarrow \infty} \theta_i = 0$. If the θ_i do not converge to zero, a new guess of θ_1 is made and the procedure is repeated. This method becomes complicated for larger values of a because in this case, for part of the range in x , θ can be a highly multiple valued function of x . In order to aid in isolating the different values of θ for a given x , it is helpful to solve the problem for, say, $n = 2, 3, 4, \dots$. Calculations have not actually been carried out as yet for $n = \infty$. The results to be presented here are for $n = 2, 3, 4$, and 5 .

It might be recalled at this point that these calculations are based on Eqs. (9), which equations were derived on the crude assumption of randomness in counting nearest neighbors. The next higher approximation would be to introduce the quasi-chemical equilibrium method. Although this method does not lead to new qualitative features when applied to monolayers, there is no assurance that the same will be true in multimolecular adsorption, though it is probably true.

In Fig. 2, we give the curves for $\epsilon_L/kT = 0$ and 2 and $n = 2, 3, 4$, and 5 . For simplicity we have taken c as very large ($\theta_1 = 1$) and considered only the part of the curves above $\theta = 1$. There is no difficulty in calculating the complete curves but the present simplification leads to curves which are independent of c (for large c —the case of most interest) and of whether or not the first layer is mobile or localized. For $\epsilon_L/kT = 0$ we have essentially the BET case and we can write

⁹ It might be remarked that Eqs. (9) can be written as a single non-linear second order difference equation with boundary conditions.

$\theta(x, n)$ explicitly. For $n = \infty$, $\theta = 1/(1-x)$. The curves for $n = 2, 3, 4$, and 5 converge toward the curve for $n = \infty$. Similarly, for $\epsilon_L/kT = 2$, the curves for $n = 2-5$ may be thought of as converging toward a curve which lies somewhat below the BET $n = \infty$ curve. It should be stated that the curves given here for $\epsilon_L/kT = 2, 3$, and 4 (Figs. 2-4) are not extremely accurate. They are, however, sufficiently exact to illustrate the essential points.

There is a symmetry property of interest for all values of ϵ_L/kT (if we take $\theta_1 = 1$): $\ln x$ is an odd function of $\theta - (n+1)/2$. This being the case we give the curves up to $\theta = 3$ only. It will be noted that the incomplete filling of capillaries at $x = 1$ in the original BET treatment (also in the modified treatment¹⁰ of Brunauer, Deming, Deming and Teller) is retained here for $\epsilon_L/kT = 2$. This is obviously related to the symmetry property mentioned above. See also Figs. 3 and 4 in this connection. However, this is not the correct approach to capillary condensation and we defer further discussion of the subject to Section IV.

Figure 3 gives similar curves for $\epsilon_L/kT = 3$. The curve for $n = 2$ is a critical curve and loops appear in the curves for $n = 3$ and $n = 4$. The $n = 5$ curve in this figure has not been calculated but just guessed (with some confidence). A BET curve is included for orientation; it is not the limiting curve. Figure 4 shows the somewhat more complicated behavior for $\epsilon_L/kT = 4$. The $n = 3$ curve is a calculated curve; it is dotted for convenience only. Below $\theta \cong 1.3$, the curves for $n = 3-5$ virtually coincide with the $n = 2$ curve. For $\theta < 2$, it can be seen how these curves are converging toward an $n = \infty$ curve. In general, such convergence seems to be faster for larger values of ϵ_L/kT . Again a BET curve is included for orientation.

There seems to be some indication in Figs. 3 and 4 that, for sufficiently large values of ϵ_L/kT , Eqs. (9) ($n = \infty$) will predict step-like adsorption. This is not certain, however, and in any case this feature may or may not be a property of a more refined set of equations. But judging from the curves calculated so far, the general behavior of Eqs. (9) for $n = \infty$ would appear to be: (1) for small $\epsilon_L/kT > 0$, $\theta(x)$ resembles the BET curve

¹⁰ S. Brunauer, L. S. Deming, W. E. Deming, and E. Teller, J. Am. Chem. Soc. 62, 1723 (1940).

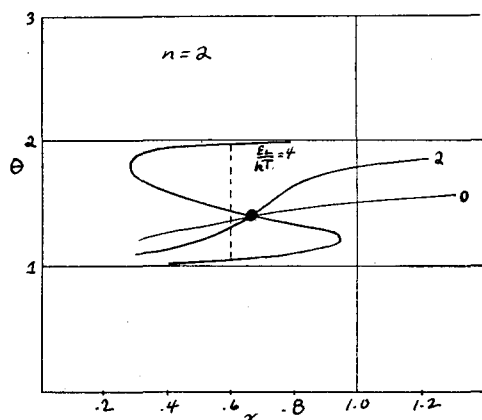


FIG. 5.

but lies below it; (2) for large ϵ_L/kT , loops appear which (a) decrease in amplitude and (b) move from $x < 1$ toward $x = 1$, as θ increases.

IV. MULTIMOLECULAR ADSORPTION BETWEEN PARALLEL WALLS

We take the same model as above, but consider that adsorption occurs between two parallel walls with room for $2n$ layers of adsorbed molecules. This model can be modified easily to apply to adsorption in cylinders or between parallel walls with $2n+1$ layers. However, we shall not discuss these systems here, since the same general arguments and results are obtained. The cylindrical equations will be of use in comparing theory with experiment since the model is more realistic.

We must now include in \mathfrak{N} a term which gives the number of pairs of nearest neighbors between molecules in the n -th and $(n+1)$ -th layers. In order to be consistent, we assume randomness; that is, we assume that the X_n molecules in each of these layers are distributed among the B sites at random and therefore without regard to the distribution in the other layer. So the probability that a molecule in the n -th layer will have a nearest neighbor in the $(n+1)$ -th layer is X_n/B . There are then X_n^2/B such pairs of neighbors. We are going to consider only layers 1 to n (since, in an equilibrium distribution, layers $2n$ to $n+1$ behave identically), so we should assign only one-half of these pairs, $\frac{1}{2}(X_n^2/B)$, to \mathfrak{N} . Equation (7) still holds here but Eq. (8) becomes

$$\mathfrak{N} = \frac{2X_1^2}{B} + \cdots + \frac{2X_{n-1}^2}{B} + \frac{5X_n^2}{2B} + N - X_1. \quad (11)$$

As a result of this modification, one finds that Eqs. (9) and (10) are unchanged except for the n -th equation which now reads

$$x = \frac{\theta_n}{\theta_{n-1} - \theta_n} \exp[a(-5\theta_n + 2)]. \quad (12)$$

The change from $4\theta_n$ to $5\theta_n$ in the exponential corresponds physically to the extra energy Q introduced by Brunauer, Deming, Deming and Teller¹⁰ in their modified BET treatment.

We give, in Figs. 5–7, a few examples based on the above model. We take c very large ($\theta_1 = 1$) in Figs. 5 and 6, but, for variety, in Fig. 7 we give the complete curve in a case with c small: $c = 1/10$. Returning to Fig. 5 ($n=2$) we see that the predicted behavior is that the first layer fills in first and then the second layer fills in suddenly and practically completely, for $\epsilon_L/kT = 4$, at about $x = 0.6$. The behavior is different for $\epsilon_L/kT = 0$ and 2. At saturation, the second layer is half full for $\epsilon_L/kT = 0$, but 0.8 full for $\epsilon_L/kT = 2$ and virtually full for $\epsilon_L/kT = 4$. All three curves pass through the point $\theta = 7/5$, $x = 2/3$. This is not, however, the center of antisymmetry. Figure 6 shows similar curves for $n=3$. For $\epsilon_L/kT = 4$, after the first layer is full, the second and third layers fill suddenly at about $x = 0.7$ or 0.8 . Comparing the $\epsilon_L/kT = 4$ case for $n=2$ (Fig. 5) and for $n=3$ (Fig. 6), we note it is predicted here that smaller capillaries fill at smaller values of x , which is in qualitative agreement with the experimental facts. Figure 7 shows how, in some cases, the complete capillary can fill suddenly, including the first layer. There are, of course, many other possible cases, but these should serve as illustrations.

It should now be clear that it is possible in principle for a single theory to include (1) multimolecular adsorption on free surfaces and in capillaries and (2) capillary condensation either with or without the first layer being adsorbed first. The multimolecular adsorption and the capillary condensation points of view are therefore really not in conflict, as has been generally assumed.

The general feature of the curves for large ϵ_L/kT which leads to capillary condensation is the following: in adsorption on a free surface the loops give the appearance of wrapping them-

selves around the $x=1$ line (as θ increases from $\theta \cong 1$); in capillary adsorption the loops tend to do the same except for the loop associated with the last layer, this "top" loop being displaced (due to the extra nearest neighbor pairs) towards smaller values of x (Fig. 6 is an illustration of this). The above can be expressed more precisely in mathematical language but the essential feature is that just described. This displacement of the top loop requires, on thermodynamic grounds (see Section V), that the phase change include *all* loops and hence the capillary is filled (except for the first layer if it is already full) virtually completely in one jump.

A further remark might be in order here. Sudden jumps of the type described will be observed experimentally only if the adsorbent has a very uniform pore structure. Generally the effect will be smoothed out due to the pore size distribution.

V. MISCELLANEOUS TOPICS*

Lattices Other than Simple Cubic

Suppose we consider a general lattice in which each site has a total of z nearest neighbor sites, z' nearest neighbor sites in the same layer and $(\xi+1)$ nearest neighbor sites in the layer above and also in the layer below:

$$z = z' + 2(\xi + 1). \quad (13)$$

The number of pairs of nearest neighbors in the

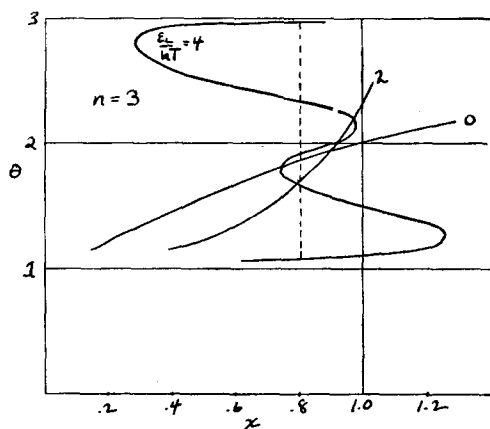


FIG. 6.

* We include in this section a brief discussion of several additional points which may be of interest.

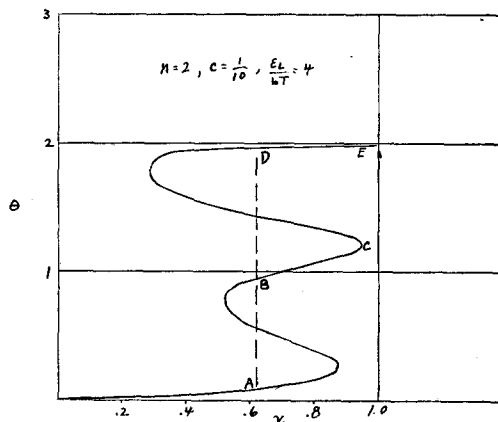


FIG. 7.

i -th layer is $(z'/2)(X_i^2/B)$. The number of pairs between the i -th and $(i+1)$ -th layers is $X_{i+1}(1 + \xi X_i/B)$. That is, each molecule in the $(i+1)$ -th layer has *at least* one nearest neighbor in the i -th layer (or the molecule could not add to the lattice—on the assumption of vertical¹¹ building), and, on the average, has $\xi X_i/B$ additional ones on the randomness assumption. In the capillary (parallel wall) case, there are an additional $[(\xi+1)/2](X_n^2/B)$ pairs to be added to \mathfrak{N} as before.

We assume that Eq. (7) still holds for all lattices. Actually, the factorial part of Eq. (7) is consistent with previous assumptions only for vertical¹² lattices (e.g., simple cubic). One can easily derive the strictly consistent factorial expression for non-vertical lattices. However, not only is it very complicated but a little reflection convinces one that, although it is consistent, it is actually probably less realistic than the original expression. At any rate, in the present discussion, we retain Eq. (7) but in place of Eq. (8) we have the more general expression,

$$\mathfrak{N} = \frac{z'}{2} \frac{X_1^2}{B} + \cdots + \frac{z'}{2} \frac{X_n^2}{B} + X_2 \left(1 + \frac{\xi X_1}{B} \right) + \cdots + X_n \left(1 + \frac{\xi X_{n-1}}{B} \right). \quad (14)$$

¹¹ By vertical building, we mean that a molecule can go into a site only if at least one nearest neighbor site in the next lower layer is already occupied. This is not the most general type of building but it is the only kind considered in this paper.

¹² By a vertical lattice we mean one in which each site is directly above a site in the next lower layer ($\xi=0$).

For the capillary case we add $[(\xi+1)/2](X_n^2/B)$ to the right hand member. One finds then, for a localized first layer,

$$\begin{aligned}
 x &= \frac{\theta_1 - \theta_2}{1 - \theta_1} \frac{1}{c} \exp[a(-z'\theta_1 - \xi\theta_2)] \\
 &= \frac{\theta_2 - \theta_3}{\theta_1 - \theta_2} \exp[a(-z'\theta_2 - \xi\theta_1 - \xi\theta_3 + z/2 - 1)] \\
 &\quad \vdots \\
 &= \frac{\theta_{n-1} - \theta_n}{\theta_{n-2} - \theta_{n-1}} \exp[a(-z'\theta_{n-1} - \xi\theta_{n-2} \\
 &\quad - \xi\theta_n + z/2 - 1)] \\
 &= \frac{\theta_n}{\theta_{n-1} - \theta_n} \exp[a(-z'\theta_n - \xi\theta_{n-1} + z/2 - 1)], \\
 a &= 2\epsilon_L/zkT.
 \end{aligned} \tag{15}$$

For a mobile first layer, it turns out that the first equation should be modified to read

$$x = \frac{\theta_1 - \theta_2}{1 - \theta_1} \frac{1}{C} \exp\left(\frac{\theta_1}{1 - \theta_1} - \alpha\theta_1 - a\xi\theta_2\right). \tag{16}$$

For adsorption between parallel walls, z' in the n -th equation should be changed according to

$$z' \rightarrow z' + \xi + 1. \tag{17}$$

The cases of special interest are:

BET:

$$z = 2, \quad z' = 0, \quad \xi = 0.$$

Simple cubic:

$$z = 6, \quad z' = 4, \quad \xi = 0. \tag{18}$$

Close packed:

$$z = 12, \quad z' = 6, \quad \xi = 2.$$

It is not correct to say that the BET theory is a special case such that $\epsilon_L/kT = 0$, for this assumption is really not made (ϵ_L/kT occurs in c). Properly, the BET treatment should be characterized as a special case as is done in Eqs. 18 (i.e. $z = 2, z' = 0; \xi$ is not an independent parameter). In Figs. 2-4, it is permissible to label the $\epsilon_L/kT = 0$ curve as the BET curve for we are considering $\theta_1 = 1$ and $\theta > 1$. The BET curve coincides for large c and $\theta > 1$.

Limitations of a Lattice-type Model

We have confined ourselves in this series of papers to a model which emphasizes a lattice structure in the adsorbate. It is possible to assign, and we have assigned, certain necessary liquid-like properties to this adsorbate. However, the model is obviously not completely satisfactory (even if it did not lead to considerable algebraic complications), because it does not become isotropic for adsorbate molecules far from the surface. A lattice model is probably best for the first several layers, but a liquid-like model would seem to be more correct otherwise. One would like to include both features in a single general model but this would no doubt be rather difficult.

What Values of ϵ_L/kT Are of Physical Significance?

In order to try to answer this question we must say something about liquids. At the same time, this will be a good opportunity to be more specific about the meaning of j_L and ϵ_L . For a perfect gas of N molecules with a volume per molecule $v = V/N$, the partition function is

$$Q = \frac{1}{N!} \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} N v j \right]^N, \tag{19}$$

where j is the internal partition function. For an imperfect gas or liquid we can write Q formally as

$$Q = \frac{1}{N!} \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} N v_f j \exp(\chi/kT) \right]^N, \tag{20}$$

in which we have replaced v by an effective "free volume" per molecule v_f and introduced an average potential energy of interaction per molecule, $-\chi$, evaluated when each molecule is in the center of its "cell." In general, we should take both v_f and χ as functions of v and T , but the relatively slight dependence of χ on T is usually ignored.

It will be noticed that in the papers of this series we have implicitly adopted

$$Q = [j_L \exp(\epsilon_L/kT)]^N \tag{21}$$

as the partition function for the liquid. Hence

the correspondence is:

$$\epsilon_L(v) = \chi(v), \quad (22)$$

$$j_L(v, T) = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} v_f(v, T) j(T) e. \quad (23)$$

If we use the harmonic oscillator model of a liquid,² Eq. (23) becomes

$$j_L(v, T) = \left(\frac{kT}{h\nu_L(v)} \right)^3 j(T) e. \quad (24)$$

We are especially interested here in $\epsilon_L(v)$. Unfortunately, there is no really satisfactory theory of liquids from which to obtain this function. However, in another paper¹³ we have calculated $\epsilon_L(v)$, approximately, from experimental $P-V-T$ data on nitrogen and argon in their respective critical regions. If we assume that the temperature dependence of ϵ_L is negligible between the boiling point and critical point, we can then estimate ϵ_L/kT not only at the critical point but also at the boiling point. It is necessary to extrapolate $1/\epsilon_L(v)$ to zero at $v=0$ in order to extend somewhat the range in v (to include the smaller value of v at the boiling point) of the critical region data. One finds then, omitting further details: (1) at the critical point, $\epsilon_L/kT = 2.1$ for nitrogen and 1.7 for argon; and (2) at the boiling point, $\epsilon_L/kT = 6.2_6$ for nitrogen and 5.7_6 for argon. The average values are 1.9 (critical point) and 6.0 (boiling point).

The above approximate values of ϵ_L/kT should not be compared in magnitude with the values in Figs. 1-7, since these figures are based on certain crude assumptions and a simple cubic lattice. However, one can make the correspondence, approximately, as follows: we find the ratio of (1) ϵ_L/kT_c based on fairly accurate considerations for localized monomolecular adsorption to (2) ϵ_L/kT_c based on the assumptions of the present paper (this value is $\epsilon_L/kT_c = 3$, from Eq. (1)), and assume that this ratio also holds for multimolecular adsorption (this assumption is consistent with a lattice-type model). We get the relatively exact value of ϵ_L/kT_c from the quasi-chemical equilibrium method, using $z=10.5$ for argon and 10.9 for nitrogen,¹³ and

taking $z'=z/2$ (i.e. we assume close packing with occasional random holes). Then,

$$\frac{\epsilon_L}{kT_c} = -\frac{z}{z'} \frac{w}{kT_c} = -2 \frac{w}{kT_c} = 2z' \ln \frac{z'}{z'-2} \cong 5.0 \quad (25)$$

for both nitrogen and argon. Equation (25) shows the connection between our ϵ_L and Fowler and Guggenheim's⁶ w , and gives ϵ_L/kT_c as a function of z' as found from the quasi-chemical equilibrium method.⁶ So we should multiply 1.9 and 6.0 (above) by approximately $\frac{3}{2}$ to convert to the ϵ_L/kT scale of Figs. 1-7. We find $\epsilon_L/kT \cong 1.1$ (critical point) and 3.6 (boiling point). The present theory is obviously applicable only below the critical temperature, or, approximately, for $\epsilon_L/kT > 1.1$. Needless to say the above approximate numerical values should not be taken too seriously. However, they seem to be the best available at the present time.

The Criticism of the BET Equation by Cassel

Cassel has pointed out⁴ that if we use the BET equation for $\Gamma(p)$ in the Gibbs equation,

$$\varphi(p) = \gamma_s - \gamma(p) = kT \int_0^p \Gamma(p) d \ln p, \quad (26)$$

where γ_s is the surface tension of the clean surface, $\gamma(p)$ is the sum of the surface tension of the adsorbate and the interfacial tension, and Γ is the surface concentration, then, for $p=p_0$, the integral becomes infinite whereas

$$\gamma_s - \gamma(p_0) = \gamma_s - \gamma_L - \gamma_{LS}$$

is certainly finite. Clearly, a correct theory should allow Γ to become infinite at $p=p_0$ but in such a way that the integral of Γ/p from $p=0$ to $p=p_0$ remains finite. Cassel attributed this failure in the BET theory to the neglect of lateral cohesion (horizontal interactions), and this certainly seems to be correct. It should be clear from Figs. 1-4 that the present treatment is in the direction of eliminating this difficulty, as expected.

Hysteresis and Capillary Condensation

As is well known, the thermodynamic theorem of equal areas is used to determine the point at which a phase change takes place when loops

¹³ T. L. Hill, J. Phys. Chem. (in press).

are encountered. This theorem is general and applies to the complicated loops found here. However, in order to apply the theorem to the adsorption isotherm, θ must be plotted as a function of $\ln x$, not x . In the figures the dotted straight lines indicate phase changes. Those parts of the solid curves which are thus skipped by a phase change are metastable if $d\theta/dx$ is positive but unstable if $d\theta/dx$ is negative. The dotted lines represent the stable equilibrium behavior.

It would seem that reversible hysteresis can be interpreted on the above basis. For example, referring to Fig. 7, one might get adsorption along $ABCE$ and desorption along EDA . There are of course other conceivable paths in both adsorption and desorption making use of metastable parts of the curve, but in every case the adsorption path is *below* (or coincides with, in the reversible stable equilibrium case) the desorption path, as is found experimentally. This follows from the condition $d\theta/dx > 0$ and because, in adsorption, the system can attain only those metastable sections of the complete curve which lie to the right of the dotted line, whereas in desorption, only metastable states to the left of the line are accessible. The same argument would apply to any other curve showing loops and capillary condensation. These effects will of course be smeared out in practice due to non-uniform pore structure.

If this argument is correct, it would not be necessary to have conical or bottle-necked capillaries to obtain hysteresis, though it may be particularly easy for capillaries of this type to get into the metastable states. From the statistical mechanical point of view, the problem of adsorption in such capillaries does not present any new features of a really fundamental nature (there are, however, new complications). There will be, as before, a single stable equilibrium curve predicted, and various metastable states possible.

Cassel⁴ has discussed hysteresis from a point of view which resembles the present one in some respects.

Use of the Quasi-Chemical Equilibrium Method

We shall indicate briefly how the quasi-chemical method might be introduced in this problem as a refinement over the random assumption. We follow the argument given in Fowler and Guggenheim⁶ for monolayers, and, for simplicity, we refer here to a simple cubic lattice with vertical building¹¹ in the lattice.

Using the same notation as above, the partition function is

$$Q = \sum_{X_1} \cdots \sum_{X_{n-1}} \sum_{\mathfrak{N}} \{g(\mathfrak{N}, N, X_1, \dots, X_{n-1}, B) \times \exp(\epsilon_L \mathfrak{N}/3kT) \times [j_s \exp(\epsilon_1/kT)]^{X_1} j_L^{N-X_1}\}, \quad (27)$$

where, for given values of N, X_1, \dots, X_{n-1} and B , $g(\mathfrak{N}, N, X_1, \dots, X_{n-1}, B)$ is the number of distinguishable configurations having \mathfrak{N} pairs of nearest neighbors. We define

$$\bar{\mathfrak{N}}(N, X_1, \dots, X_{n-1}, B, \epsilon_L/kT)$$

and

$$\mathfrak{N}'(N, X_1, \dots, X_{n-1}, B, \epsilon_L/kT)$$

by the following equations:

$$\begin{aligned} \bar{\mathfrak{N}} &= \sum_{\mathfrak{N}} g(\mathfrak{N}, N, X_1, \dots, X_{n-1}, B) \times \exp(\epsilon_L \mathfrak{N}/3kT) \\ &= \sum_{\mathfrak{N}} \mathfrak{N} g(\mathfrak{N}, N, X_1, \dots, X_{n-1}, B) \times \exp(\epsilon_L \mathfrak{N}/3kT), \quad (28) \\ \mathfrak{N}' &= \sum_{\mathfrak{N}} g(\mathfrak{N}, N, X_1, \dots, X_{n-1}, B) \exp(\epsilon_L \mathfrak{N}/3kT) \\ &= \frac{\exp(\epsilon_L \mathfrak{N}'/3kT) B!}{(B-X_1)!(X_1-X_2)! \cdots (X_{n-1}-X_n)! X_n!}, \quad (29) \end{aligned}$$

where

$$\begin{aligned} X_n &= N - (X_1 + \cdots + X_{n-1}) \\ \sum_{\mathfrak{N}} g(\mathfrak{N}, N, X_1, \dots, X_{n-1}, B) &= \frac{B!}{(B-X_1)! \cdots (X_{n-1}-X_n)! X_n!}. \quad (30) \end{aligned}$$

We see from Eqs. (27) and (29) that

$$Q = \sum_{X_1} \cdots \sum_{X_{n-1}} \left\{ \frac{[j_s \exp(\epsilon_1/kT)]^{X_1} j_L^{N-X_1} B! \exp(\epsilon_L \mathfrak{N}'/3kT)}{(B-X_1)!(X_1-X_2)! \cdots (X_{n-1}-X_n)! X_n!} \right\}. \quad (31)$$

One can also show, as usual, that

$$\bar{\mathfrak{N}} = -T^2 \frac{\partial(\mathfrak{N}'/T)}{\partial T}, \quad (32)$$

and that the contribution of the molecular interactions to the free energy is $-\epsilon_L \mathfrak{N}'/3$ and the contribution to the internal energy is $-\epsilon_L \bar{\mathfrak{N}}/3$. If $\bar{\mathfrak{N}}$ (and therefore \mathfrak{N}') is independent of temperature, $\bar{\mathfrak{N}} = \mathfrak{N}'$. $\bar{\mathfrak{N}}$ is the ordinary statistical average value of \mathfrak{N} .

On the random assumption, $\bar{\mathfrak{N}}$ is independent of temperature, $\bar{\mathfrak{N}} = \mathfrak{N}'$, and hence Eq. (7) was used correctly. But the correct equation of more general validity is Eq. (31).

Equations (8) and (11) give the random approximation to $\bar{\mathfrak{N}}$ for the case we are discussing. The average number of horizontal interactions in the first layer is $2B\theta_1^2$, where $\theta_i = X_i/B$. The quasi-chemical method⁶ gives, as a better approximation,

$$\bar{\mathfrak{N}}_1 = 2B\theta_1^2[1], \quad (33)$$

$$[i] = \frac{\beta_i - 1 + 2\theta_i}{\theta_i(\beta_i + 1)}, \quad (34)$$

$$\beta_i = \{1 - 4\theta_i(1 - \theta_i)[1 - \exp(\epsilon_L/3kT)]\}^{1/2}. \quad (35)$$

The ratio R_1 of the refined to the crude value is $R_1 = [1]$. When $\epsilon_L/kT = 0$, $\beta_1 = [1] = R_1 = 1$. The X_2 molecules of the second layer are distributed on top of the X_1 molecules of the first layer. In the case of attraction ($\epsilon_L/kT > 0$) there is a

tendency for the first layer molecules to cluster (horizontally), according to Eq. (33). Therefore, even if the second layer molecules were distributed completely at random on the available sites (the first layer molecules), the same clustering factor $[1]$ would persist in the second layer. But we do not expect a random distribution of X_2 on X_1 ; there should be an additional tendency to cluster due to the interactions between the X_2 molecules themselves. We assume that the correcting factor, in analogy with the situation in the first layer, is $R_2 = [2]$. Extending this type of argument (it applies for any value of ϵ_L/kT), we find, in place of Eq. (8),

$$\begin{aligned} \bar{\mathfrak{N}} = & 2B\theta_1^2[1] + 2B\theta_2^2[1][2] + \cdots \\ & + 2B\theta_n^2[1][2] \cdots [n] + N - X_1. \end{aligned} \quad (36)$$

In order to be consistent, in the case of adsorption between two parallel walls, we should assume a quasi-chemical equilibrium in counting the number of vertical pairs of nearest neighbors between the n -th and $(n+1)$ -th layers. On applying the quasi-chemical argument to this system of sites and occupied sites, one finds that the number is $B\theta_n^2[n]$. So for capillary adsorption, we add $\frac{1}{2}B\theta_n^2[n]$ to $\bar{\mathfrak{N}}$ in Eq. (36).

The next step is to obtain \mathfrak{N}' from $\bar{\mathfrak{N}}$ by integrating Eq. (32). One then substitutes \mathfrak{N}' into Eq. (31) to obtain Q . Q is then used as before. Unfortunately, it appears that these steps can be carried out explicitly only for the very simplest cases.