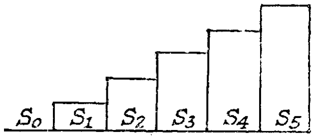
201. *The Sorption of Condensable Vapours by Porous Solids. Part III. Multimolecular Adsorption.*

By A. Graham Foster.

A simplified derivation of the general equations of the Brunauer theory of multimolecular adsorption is followed by a discussion of the application of this theory to abnormal types of isothermal.

Adam has recently drawn attention (*Nature*, 1945, **155**, 154) to the merits of the theory of multimolecular adsorption put forward by Brunauer and his collaborators (*J. Amer. Chem. Soc.*, 1938, **60**, 309). It is remarkable that a general theory of adsorption which claims to account for all observed types of isothermal should have attracted comparatively little notice in this country, but, unfortunately, the equations to which this theory finally leads are complex, and one of the fundamental assumptions, *viz.*, that the net heat of sorption falls to zero after the completion of the first layer, is contrary to experimental fact. However, the theory has been remarkably successful in accounting for the main types of sorption isothermal, although the authors have not discussed in detail just how this is achieved; they merely show that, by assigning suitable values to the constants of their equations, it is possible to obtain curves which approximate to the various known types of isothermal. A simplified derivation of the theory is now given, followed by an examination of what may be regarded as the " limiting cases " of the general equation, thus making clear why the theory is so successful in explaining the so-called " abnormal " types of isothermal. In Part IV the application of the theory to linear isothermals is discussed in some detail.

FIG. 1.



Derivation of the General Equation.—Langmuir, in the classical paper in which he first presented the theory of unimolecular adsorption (*J. Amer. Chem. Soc.*, 1918, **40**, 1361), also discussed the possibility of multilayer adsorption, and derived a complex equation which Brunauer has simplified by making the rather drastic assumption that the net heat of sorption falls to zero after the first layer is completed. In considering the evaporation–condensation equilibria for the second layer, Langmuir supposed that condensation occurred on the uncovered portion of the first layer and that evaporation from the latter took place from that part which was not itself covered by the second layer. The various layers, being in equilibrium with the gas phase, are necessarily in equilibrium with one another, so that, as pointed out by Brunauer, it is unnecessary to consider exchanges of adsorbed molecules between the various layers. If we denote the fractions of the total surface covered by 0, 1, 2, etc., layers by s_0, s_1, s_2, etc., as in Fig. 1, and equate rates of condensation and evaporation for each layer, we obtain a series of equations of the type $\alpha_1 p s_0 = \beta_1 s_1$; $\alpha_2 p s_1 = \beta_2 s_2$, etc., or, replacing α/β by a single constant c, we have for the nth layer $c_n p s_{n-1} = s_n$, whence

$$s_n = (c_n \,.\, c_{n-1} \,.\, c_{n-2} \;.\;.\;.\;.\; c_2 c_1) s_0 p^n$$

The total adsorption a, expressed as a fraction or multiple of the amount required to form a complete unimolecular layer, is then given by $a = s_1 + 2s_2 + 3s_3 \;.\;.\;.\;. + ns_n$, and the additional relation $s_0 + s_1 + s_2 + s_n = 1$ enables us to express a as a function of p :

$$a = c_1 p s_0 + 2c_1 c_2 p^2 s_0 + 3c_1 c_2 c_3 p^3 s_0 \;.\;.\;.\;.\; nc_1 c_2 c_3 \;.\;.\;.\;.\; c_{n-1} c_n p^n s_0$$
$$1 = s_0 + c_1 p s_0 + c_1 c_2 p^2 s_0 + c_1 c_2 c_3 p^3 s_0 + \;.\;.\;.\;. + c_1 c_2 c_3 \;.\;.\;.\;.\; c_n p^n s_0$$

whence

$$a = (c_1 p + 2c_1 c_2 p^2 + 3c_1 c_2 c_3 p^3 + \;.\;.\;.\;. + nc_1 c_2 c_3 \ldots c_n p^n)/(1 + c_1 p + c_1 c_2 p^2 + c_1 c_2 c_3 p^3 \;.\;.\;.\;. + c_1 c_2 c_3 \ldots c_n p^n) \quad . \quad (1)$$

The essential feature of Brunauer's treatment lies in the development of Langmuir's suggestion that this relation could be simplified by putting $c_2 = c_3$, etc. We then get

$$a = c_1 p(1 + 2x + 3x^2 \;.\;.\;.\;. + nx^{n-1})/\{1 + c_1 p(1 + x + x^2 \;.\;.\;.\; x^{n-1})\} \;.\quad .\quad .\quad (2)$$

where $x = c_2 p$ and it is now possible to sum both series to $n - 1$ terms (or to infinity, if $x < 1$), since the lower series is a geometrical progression and the upper series is its differential. Equation (2) is really the simplest form of the multilayer theory. The summation of the two series, although desirable in order to facilitate computation when n is large, is not essential, and, as shown by Brunauer, results in the less easily remembered form

$$a = cx\{1 - (n + 1)x^n + nx^{n+1}\}/(1 - x)\{1 + (c - 1)x - cx^{n+1}\} \quad .\quad .\quad .\quad .\quad (3)$$

(where $c_1 p$ has been replaced by cx to conform with his notation; *i.e.*, $c = c_1/c_2$).

The author has already shown (this vol., p. 364) that the constant c_1 of the Langmuir equation may be expressed approximately in the form

$$c_1 p_0 = e^{Q/\boldsymbol{R}T} \quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad (4)$$

where Q is the net heat of sorption and p_0 the saturation pressure. This relation is strictly valid only when the partition functions of the adsorbed and the liquid state are identical, a condition more likely to be fulfilled in the second and subsequent layers than in the first. The same condition is implicit in Brunauer's assumption that the evaporation–condensation properties of the molecules in the second and higher layers are identical with those of the bulk liquid. The direct introduction of equation (4) as an alternative to Brunauer's kinetic treatment enables the final result to be reached more rapidly. The crucial point of Brunauer's theory is that Q is put equal to zero for all layers after the first, *i.e.*, the total heat of sorption is assumed to be equal to heat of condensation. This makes $c_2 = 1/p_0$ and $x = p/p_0$, the relative pressure, which is always less than unity, and thus enables the series to be summed to infinity if necessary. One important consequence of this assumption seems to have been overlooked by the authors, namely, that a layer for which $Q = 0$ can never be more than half saturated. For instance, in the simple Langmuir equation $a = c_1 p/(1 + c_1 p)$ it is evident that if $c_1 = 1/p_0$ then $a = x/(1 + x)$, and when $x = 1$, $a = \frac{1}{2}$. A similar effect appears in equation (2), since when

$x = 1$ we find $a = cx(1 + 2 + 3 + 4 + \ldots . + n)/(1 + ncx)$. As cx increases, $cx/(1 + cx)$ approaches unity and $a = (1 + 2 + 3 + 4 + \ldots . + n)/n = n(n + 1)/2n = (n + 1)/2$ or $(n - 1)/2 + 1$; *i.e.*, beyond the first layer, the total adsorption space is only half filled even when the saturation pressure is reached.

Limiting Cases of the General Equation.—In special cases a further simplification of equation (2) is possible. (i) When n becomes infinite the well-known expression for the sum to infinity of a geometrical series enables us to write

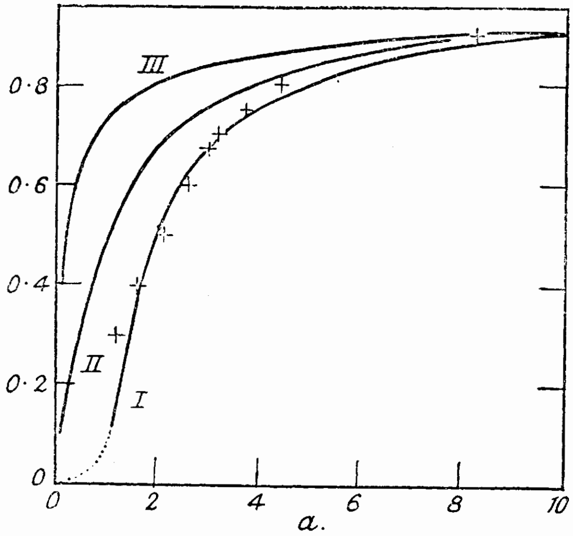
$$a = cx/(1 - x)(1 - x + cx) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

provided of course that x be really <1 (or Q zero). Now, according to Brunauer, this expression is not very different from equation (3) when $n > 5$ (Fig. 3 shows that this is so for values of $x < \frac{1}{2}$), and its use leads to the fairly simple equation

$$p/a(p_0 - p) = 1/c + (p/p_0)(c - 1)/c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

according to which the function on the left should give a linear plot against p from which the constant c can be evaluated. Unfortunately, in the absence of low-pressure data, the amount required to form a unimolecular layer (v_m) will also be unknown, and a must be replaced by v/v_m, where v is the actual amount adsorbed at pressure p. The function $p/v(p_0 - p)$ is then plotted against p/p_0, the slope being equal to $(1/v_m)(c - 1)/c$, and the intercept equal to $1/cv_m$, whence both unknowns, c and v_m, may be determined. At low pressures and large values of c, equation (6) reduces to the Langmuir equation, giving a linear plot of p/v against p.

FIG. 2.



(ii) When the first layer is strongly held, c is large, and when cx is also large compared with $(1 - x)$, equation (5) reduces to

$$a = cx/(1 - x)cx \text{ or } a = 1/(1 - x) \quad . \quad (7)$$

and we find the adsorption following the Langmuir equation at very low pressures but at higher pressures following an equation which gives an isotherm convex to the pressure axis (curve I, Fig. 2). Isothermals of this type are known, but direct application of equation (7) is usually rendered difficult by the absence of accurate data at low pressures from which to calculate the amount held in the first layer (*i.e.*, to determine what concentration corresponds to $a = 1$). It is, however, possible to evaluate this quantity from the higher-pressure data alone if equation (7) is valid, because the concentrations at which $x = \frac{1}{2}$ or $\frac{2}{3}$ should correspond to $a = 2$ or 3, respectively. The observed concentrations are then divided by the amount presumed to be held in the first layer, and the actual pressures converted into relative pressures in order to obtain the $a - x$ curve. Lambert and Foster's data (*Proc. Roy. Soc.*, 1932, *A*, **136**, 363) for benzene on ferric oxide, treated in this way, give the points represented by the crosses in Fig. 2, which approximate to the actual graph of equation (7). The observed net heat of sorption is only 3 cals./g. over this range, compared with 100 cals. for the latent heat of condensation, so that the assumption that $Q = 0$ is almost justified for this system. On the other hand, the data for ethyl alcohol on the same adsorbent show poor agreement with equation (7). Reasonable agreement is found with water on copper oxide but not on manganese oxide, Bray and Draper's data (*Proc. Nat. Acad. Sci.*, 1926, **12**, 295) being used. Bangham and Mosallam's data (*Proc. Roy. Soc.*, 1938, *A*, **165**, 552) for the adsorption of benzene on plane surfaces of mica might be expected to provide a more favourable test of equation (7), but the agreement is only moderate. If this equation were of general validity at high relative pressures it would of course be possible to reduce all isothermals to the same scale by converting actual pressures into relative pressures and concentrations to a values.

(iii) Another interesting case arises when $c = 1$ (or $Q = 0$), for then

$$a = x/(1 - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

over the entire range, giving an isothermal convex to the p axis as shown in Fig. 2, curve II. As Brunauer points out, this particular case appears to have been realised experimentally by Reyerson and Cameron (*J. Physical Chem.*, 1935, **39**, 181) with bromine on silica gel. Since $x = \frac{1}{2}$ when $a = 1$, Brunauer was able to calculate the theoretical maximum sorption in the first layer, and hence the surface area of the gel was found to be 470 m.^{2}/g., agreeing well with the mean value of 500 calculated by different methods from the isothermals of more complex types given by gases on the same gel at low temperatures.

(iv) Finally, the multilayer theory requires that adsorption shall still take place, even if the net heat of sorption is negative. When $c \ll 1$ we find

$$a = cx/(1 - x)(1 - x) = cx/(1 - x)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

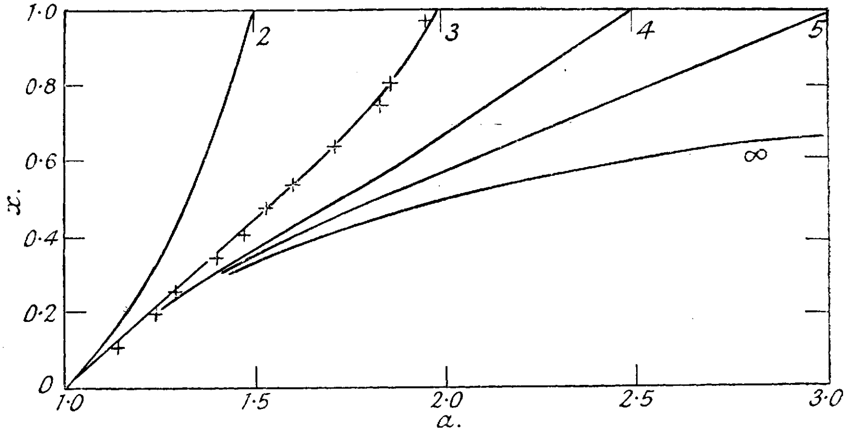
A plot of this function when $c = 1/10$ is shown in curve III of Fig. 2. As yet, this extreme type of isothermal does not appear to have been realised experimentally.

Linear Isothermals.—Brunauer and his collaborators do not appear to have considered the interesting case which arises when n has the values 2 or 3, for the theory then leads directly to an explanation of the peculiar isothermals given by the alcohols on silica gels (Foster, *Proc. Roy. Soc.*, 1934, *A*, **146**, 129); *e.g.*, the isothermal of ethyl alcohol on silica gel B shows a linear middle portion which follows an extensive region of low-pressure sorption and extends almost to saturation. If in equation (1) we put $c_2 = c_3$, $n = 3$, and make c large, we find

$$a = (1 + 2x + 3x^2)/(1 + x + x^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where, although x is still equal to c_2p, it is not necessarily equal to the relative pressure, because q is not necessarily zero for the second and the third layer. This function, shown in Fig. 3, gives a curve of the same shape as the alcohol isothermal just mentioned, the linear part of which extrapolates back to zero pressure at about 150 mg./g., so that the a values may be calculated by dividing actual concentrations by 150. The crosses in Fig. 3 were obtained by plotting these a values against $p/40$, instead of $p/60$ as required if $c_2 = 1/p_0$. The agreement is striking, and since the isothermals of the other alcohols can be reduced to the same scale in a similar manner (as shown in Part IV), it suggests that the linear isothermal does really represent the building up of a second and a third layer on top of the more strongly held first layer. In the simpler case where $n = 2$, the terms in x^2 vanish, leaving

FIG. 3.



$$a = cx(1 + 2x)/[1 + cx(1 + x)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If c is put equal to 10 and $x = p/20$ (instead of $p/35$ for $x = p/p_0$), an excellent agreement is obtained with the isothermal of ethyl alcohol on silica gel *A* determined by Lambert and Foster (*Proc. Roy. Soc.*, 1931, *A*, **134**, 246). The application of the theory to linear isothermals is considered in more detail in Part IV.

Determination of Surface Area of Adsorbents.—Shortly after the discovery of these linear isothermals, Brunauer and Emmett (*J. Amer. Chem. Soc.*, 1935, **57**, 1754) investigated the sorption of gases at low temperatures on iron catalysts and obtained S-shaped isothermals with an intermediate linear portion. At first it was thought that the extrapolation of the linear part to zero pressure, called " point A," corresponded to the volume of gas required to cover the surface with a unimolecular layer, but later, better agreement was found by taking " point B " at which the linear isothermal begins. The applications of this method have been described in some detail (Brunauer, " Physical Adsorption of Gases," Oxford, 1944) and it is shown that the theory of multimolecular adsorption provides methods for calculating the surface areas from all types of isothermal. From Fig. 3, where $a - x$ curves for equation (10) are plotted for $n = 2, 3, 4,$ and 5 and also $n = \infty$, it will be seen that when $n > 3$ the curves become convex to the x axis and the straight part tends to vanish. As c decreases, the curves no longer extrapolate back to $a = 1$ at low pressures, but become concave to the x axis and approach the origin at $a = 0$. The combined effect of these two factors may easily create an intermediate linear range on an isothermal for which $n > 3$, which does not extrapolate back to $a = 1$, so that no theoretical significance can be attached to " point B " since its location will depend on the value of c, and the greater the magnitude of c the closer will "point B" approach "point A." The agreement between the saturation values derived from the Langmuir equation and the " point A " values is discussed in Part IV.

Finally, it should be emphasised that the new theory, unlike the older " potential " theories of multilayer adsorption put forward by Eucken and Polanyi, does not postulate the existence of long-range adsorptive forces, but is consistent with Langmuir's views on the short range of these forces. Adsorption beyond the first layer takes place under the influence of the cohesive forces of the molecules of the adsorbed substance acting as in the liquid state, so that a fraction of the surface must always be covered with a layer more than one molecule thick except at very low pressures, or above the critical temperature, or in pores too narrow to admit a second layer. Although the new theory gives a satisfactory explanation of S-shaped isothermals without assuming that capillary condensation occurs, it should be regarded as complementary to, rather than as superseding, the capillary theory.

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