245. *The Adsorption Isotherm of Langmuir and of Brunauer, Emmett, and Teller for Multilayers where* n *is* 2.

By D. C. Jones and E. W. Birks.

An analysis of the adsorption isotherm of Langmuir and of Brunauer, Emmett, and Teller (B.E.T.) for multilayers where the number of such layers is limited to two is made. The *realisable* isotherms show interesting changes of type as σ_1/σ_2 or c reaches certain critical values, σ_1 and σ_2 being the relative lives of adsorbed molecules in the first and second layers respectively : the B.E.T. assumption, that $\sigma_2 = \sigma_{\text{liquid}}$, need not be made in this case. For $c = 4$ the isotherm is a rectangular hyperbola, passing through the origin and therefore, for this case, bilayer adsorption on this model gives an isotherm of the same form as that given by the Langmuir monolayer equation. Deviations from the hyperbola occur as $c \gtrless 4$ and the deviations are simply related to the value of c.

One of the authors has pointed out (Jones *et al.*, *J.*, 1951, 126) the resemblances existing between the Brunauer–Emmett–Teller equations for multilayer adsorption and those of Langmuir (*J. Amer. Chem. Soc.*, 1918, **40**, 1361) for Cases IV and VI, which are concerned, respectively, with adsorption where n molecules can occupy one elementary space and where multilayers, in limited numbers up to n, or where n is infinite, can occur.

Equation 1 is essentially that of Langmuir for Case IV where η is the total quantity of adsorbed gas expressed in g.-mols., $\boldsymbol{N}$ is Avogadro's number, N_0 is the number of elementary spaces per sq. cm., μ is the collision number, and $\sigma_1, \sigma_2 \ldots\ldots \sigma_n$ are the relative lives of the adsorbed molecules in the elementary spaces containing 1—n molecules.

$$\frac{\boldsymbol{N}}{N_0}\eta = \frac{\sigma_1\mu + 2\sigma_1\sigma_2\mu^2 + 3\sigma_1\sigma_2\sigma_3\mu^3 + \ldots\ldots\ldots}{1 + \sigma_1\mu + \sigma_1\sigma_2\mu^2 + \sigma_1\sigma_2\sigma_3\mu^3 + \ldots\ldots} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If now the Langmuir assumption is made that $\sigma_1 \neq \sigma_2$ but that $\sigma_2 = \sigma_3 = \sigma_4$, etc., then equation 1 becomes :

$$\frac{\boldsymbol{N}}{N_0}\eta = \frac{\sigma_1\mu[1 + 2(\sigma_2\mu) + 3(\sigma_2\mu)^2 + \ldots . n(\sigma_2\mu)^{n-1}]}{1 + \sigma_1\mu[1 + (\sigma_2\mu) + (\sigma_2\mu)^2 + \ldots (\sigma_2\mu)^{n-1}]} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The corresponding equation given by Brunauer ("The Adsorption of Gases and Vapours," Oxford Univ. Press, 1945) is

$$\frac{V}{V_m} = \frac{cx}{1-x} \cdot \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (c-1)x - cx^{n+1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$= \frac{cx}{1-x} \cdot \frac{(1-x)^2(1 + 2x + 3x^2 + \ldots\ldots . nx^{n-1})}{(1-x)[1 + cx\,(1 + x + x^2 + \ldots x^{n-1})]} \quad . \quad . \quad . \quad . \quad (4)$$

$$= \frac{cx(1 + 2x + 3x^2 + \ldots\ldots nx^{n-1})}{1 + cx\,(1 + x + x^2 + \ldots\ldots x^{n-1})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Comparing equations 2 and 5 it is seen that they are identical if $\sigma_1\mu = cx$, and $\sigma_2\mu = x$: the quantity $c = \sigma_1/\sigma_2$, the ratio of the relative lives of the adsorbate on the first and on the subsequent layers (*vide* Jones, *loc. cit.*).

Consideration of the case for $n = 3$ and the general case will be dealt with in further papers. In this communication the case for $n = 2$ is analysed. This has especial interest because (1) it has been reported to occur experimentally; (2) no assumptions need be made as to the value assigned to σ_2 (in the B.E.T. theory $\sigma_2 = \sigma_L$ where σ_L is the relative life of the adsorbed molecule on the liquid surface) : so that this objection to the B.E.T. theory is not present in this case; (3) the analysis would also apply to the case where a monolayer is not exceeded but where *two* molecules can be present per elementary space.

Using the B.E.T. nomenclature but remembering that c is now σ_1/σ_2 and has not the special significance allotted to it by these authors, we have, from equation 5 :

$$\frac{V}{V_m} = \frac{cx(1 + 2x)}{1 + cx + cx^2} \qquad (6)$$

$$\frac{1}{c} \cdot \frac{\mathrm{d}(V/V_m)}{\mathrm{d}x} = \frac{1 + 4x + cx^2}{(1 + cx + cx^2)^2} \qquad (7)$$

$$\frac{1}{c} \cdot \frac{\mathrm{d}^2(V/V_m)}{\mathrm{d}x^2} = \frac{2[(2 - c) - 3cx - 6cx^2 - c^2x^3]}{(1 + cx + cx^2)^3} \qquad (8)$$

The conclusions that will be drawn as regards the main features of the isotherm are illustrated in Figs. 1 *A*, *B*, and *C*, these sections of the figure referring to the cases $c > 4$, $c = 4$, and $c < 4$ respectively.

Equation 6 gives $V/V_m = 0$ if $x = 0$; $V/V_m = 0$ also for $x = -1/2$ except where $c = 4$. All the isotherms therefore pass through the origin and through the point ($V/V_m = 0$, $x = -1/2$) with this exception. In the case of $c = 4$ equation 6 becomes $V/V_m = 4x/(1 + 2x)$, which is a rectangular hyperbola with asymptotes $V/V_m = 2$ and $x = -1/2$ (Fig. 1 *B*).

FIG. 1 *A*.

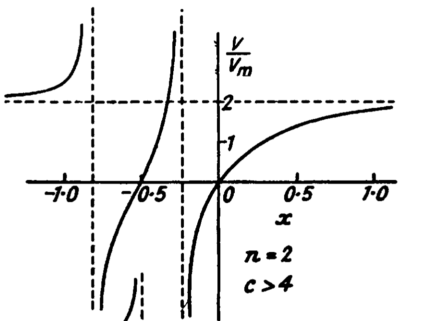
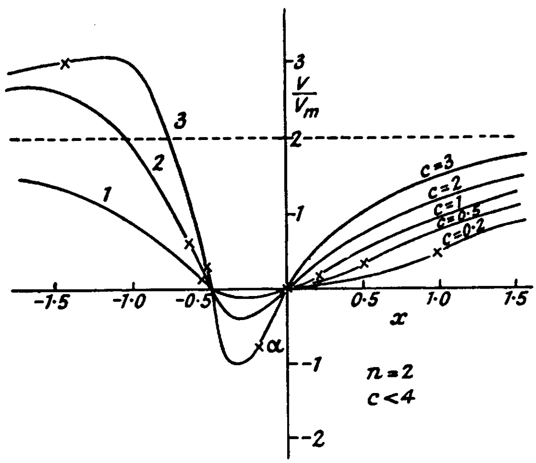


FIG. 1 *C*.



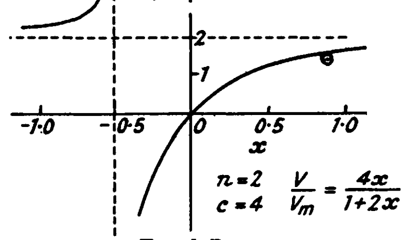


FIG. 1 *B*.

$V/V_m = \infty$ if $cx^2 + cx + 1 = 0$: it is readily seen that if $c > 4$ there are two real negative roots to this equation, *i.e.*, there are *two* asymptotes for negative values of x; these asymptotes approach each other as c diminishes; when $c = 4$ the asymptotes coincide at $x = -1/2$ (two equal roots) (Fig. 1 *B*) if $0 < c < 4$ the roots are imaginary.

Again, V/V_m approaches 2 as x approaches infinity; indeed, as can be deduced from equation 5, in general, V/V_m approaches n asymptotically as x approaches infinity; this of course also applies to the well-known Case 1 of Langmuir where $n = 1$.

From equation 7 it can be shown that there are no turning values if x is positive, or, if x is negative, when $c > 4$ (Fig. 1 *A*); there are two turning points if $c < 4$, at negative values of x, the curves having a maximum and a minimum, but only one asymptote, $V/V_m = 2$ (Fig. 1 *C*). When $c = 4$

$$\frac{\mathrm{d}(V/V_m)}{\mathrm{d}x} = \frac{c}{1 + 4x + 4x^2} = \frac{c}{(1 + 2x)^2} = \infty \text{ if } x = -\tfrac{1}{2}.$$

The gradient is thus ∞ at $x = -1/2$ and has finite values if x is $>$ or $< -1/2$ (Fig. 1 *B*).

The slope at the origin for all isotherms is c.

The roots of the cubic equation comprising the numerator of equation 8 have been determined by the cosine method and confirm that when $4 > c > 2$ there are three *negative* points of inflection; when $c = 2$ there are two negative points of inflection and *one* at the origin;

when $c < 2$ two points of inflection are negative and the third is now positive; when c has the values 1, 0·5, and 0·2, the corresponding positive points of inflection are, approximately, at the values of $x = 0{\cdot}22$, 0·5, and 1, respectively. The points of inflection on the curves shown are marked by crosses in Fig. 1 *C*. The negative point of inflection marked α in Fig. 1 *C* near the minimum of the curve for $c = 3$, moves to the origin when $c = 2$, and then occurs at higher positive values of x as the value of c diminishes.

It will be noticed that the numerator of equation 8 contains a term independent of x, *viz.*, $(2 - c)$. Further analysis has shown that this constant term is present whatever the value of n $(n > 1)$; it is characteristic of this Langmuir multilayer model. It follows that when $c = 2$ there is always a point of inflection at the origin and this means that a change of adsorption type occurs always at this value of c in this model. This type change is heralded by corresponding changes in the shapes of the isotherms. This can be seen clearly from the realisable isotherms shown in Fig. 2, and the corresponding $x/(V/V_m)$ against x plots given in Fig. 3.

FIG. 2.

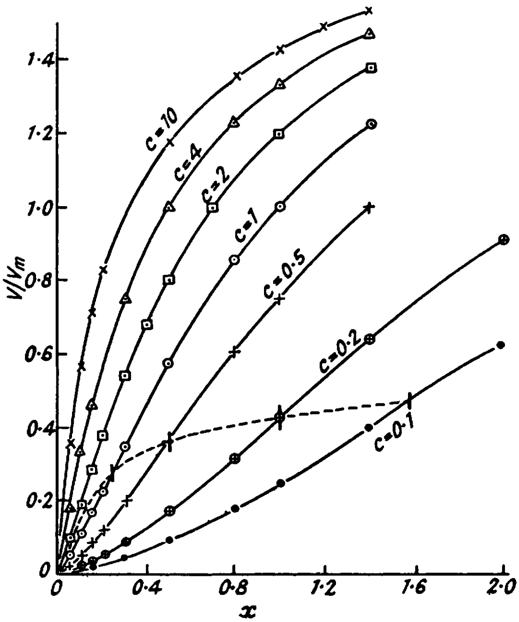
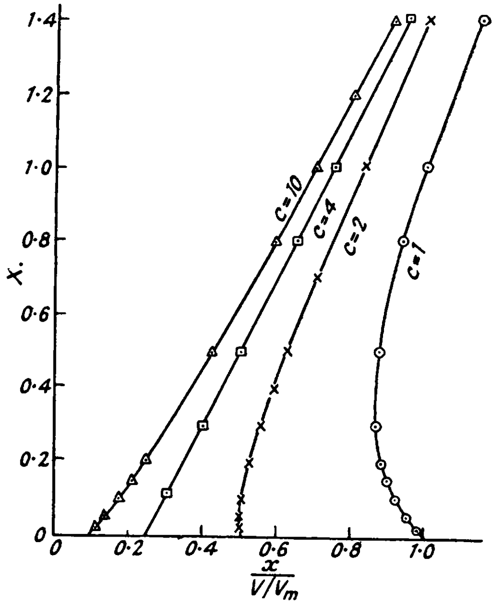


FIG. 3.



For $c = 4$ the isotherm is a rectangular hyperbola passing through the origin; this equation is of the same character as that for Langmuir's Case 1, and, as seen in Fig. 3, a straight line is obtained in this case.

If $c > 4$ there are deviations from the linear relation, *e.g.*, $c = 10$ in Fig. 3, and, if $c < 4$ much greater deviations, but now in the opposite direction, *e.g.*, $c = 1$ and 2 in Fig. 3. The corresponding changes in the shapes of the isotherms can be seen in Fig. 2; the almost linear portion for $c = 2$ found occurring from the origin to values of $x = 0{\cdot}3$ (approx.) and even to higher values of x for $c = 1$, is due to the position of the point of inflection whose locus is indicated by a broken line in the diagram. These linear portions give slopes approximately equal to the initial slope c. It may be noticed that although for this case of $n = 2$, only when $c = 4$ would the curve give a true straight line plot as in Fig. 3, yet deviations would not be large for neighbouring values of c, and further, even in the range from $c = 10$ to $c = 1$, extrapolation of the plot at low values of x to $x = 0$ would give fairly accurately the value of $1/c$ (see Fig. 3). Thus from equation 6

$$\frac{x}{V/V_m} = \frac{1}{c}\cdot\frac{1 + cx + cx^2}{1 + 2x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$= \frac{1 + 2x}{4} + \frac{\frac{4}{c} - 1}{4(1 + 2x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

From equation 9 it is seen that the function $x/(V/V_m) = 1/c$ when $x = 0$. The transformation in equation 10 gives the deviation of the function from the case of $c = 4$ (the hyperbola); the first term on the right-hand side of equation 10 is the value of the function for $c = 4$, and the second term gives the deviations, which are negative or positive as $c >$ or < 4 : further, when c is large the numerator of the second term approaches the value -1 and the deviations approach a constant value for each value of x; also the deviation becomes greater for a given value of c as x approaches 0. These points have illustrations in Fig. 3 and may be useful in the interpretation of experimental results.

In this case then, the *realisable* adsorption curves are of type I if $c > 2$ (interpreting type I as the isotherm which is always concave downwards and not necessarily obeying the Langmuir Case 1 equation); type V if $0{\cdot}2$ (approx.) $< c < 2$. If $0 < c < 0{\cdot}2$ (approx.), the positive point of inflection is at values of $x > 1$ and the adsorption type could perhaps best be called VA, although it resembles type III in being convex downwards for the whole of the *realisable* curve.

Queen Mary College, University of London. [*Received, January* 12*th*, 1951.]