28. *Some Comments on the B.E.T. (Brunauer–Emmett–Teller) Adsorption Equation.*

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The B.E.T. (Brunauer–Emmett–Teller) adsorption equation is compared with Langmuir's Cases IV and VI. An analysis of the equation leads to corrected conditions for the occurrence of adsorption curves of types II and III. The locus of the points of inflection realisable in type II curves is investigated.

GREAT interest has been aroused in the B.E.T. (Brunauer–Emmett–Teller) equation which was derived by application of the usual Langmuir kinetic method to multimolecular adsorption on a free surface. The theory was then extended in an interesting way to adsorption in capillaries where the diameter of the capillary provided a mechanical obstruction to the development of more than a limited number of adsorbed layers, and also to capillary condensation.

It is, however, often forgotten that Langmuir himself, in his well-known paper (*J. Amer. Chem. Soc.*, 1918, **40**, 1361) visualised and formulated an equation to cover the case of adsorbed films more than one molecule thick, which he labelled Case VI, and in which he made the same assumption which later Brunauer, Emmett, and Teller (Brunauer, "The Adsorption of Gases and Vapours," Oxford Univ. Press, 1945) made in order to arrive at their equations for adsorption on a free surface. The development of the equations differs somewhat, but the same result is obtained although it is expressed in different terms. In the present paper the two methods are briefly compared and a closer study is then made of the form of the theoretical adsorption curves.

Langmuir (*loc. cit.*) showed that the equation obtained for Case VI is identical with that obtained for his Case IV, in which each elementary space is assumed to hold more than one adsorbed molecule and the rate of evaporation is dependent on the number of adsorbed molecules present per elementary space. In Case IV, ν_n represents the rate of evaporation from elementary spaces containing n molecules, α_n is the reflection coefficient corresponding to spaces containing $(n - 1)$ molecules and σ_n $(\equiv \alpha_n/\nu_n)$ is the corresponding relative life. The development is now as in Langmuir's Case I: when equilibrium is reached the rate of evaporation from that fraction of the surface containing elementary spaces with the same number of molecules is balanced by the rate of condensation in such spaces; the equation obtained at equilibrium is

$$\frac{\boldsymbol{N}}{N_0}\eta = \frac{\sigma_1\mu + 2\sigma_1\sigma_2\mu^2 + 3\sigma_1\sigma_2\sigma_3\mu^3 + \ldots .}{1 + \sigma_1\mu + \sigma_1\sigma_2\mu^2 + \sigma_1\sigma_2\sigma_3\mu^3 + \ldots .} \quad . \quad . \quad . \quad . \quad . \quad (26)$$

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 $\sigma_1, \sigma_2 \ldots \sigma_n$ are the relative lives of the adsorbed molecules in the elementary spaces containing 1—n molecules. In Case VI, where multilayers are presumed to occur, ν_n is the rate of evaporation from the nth layer, and α_n the reflection coefficient of molecules striking the $(n - 1)$th layer. If we "assume each elementary space holds one molecule only, the problem is then identical with Case IV . . . . and a solution of the problem is given by Eq. 26." Langmuir's treatment is now to take out σ_1 from the numerator of equation (26) and to divide both numerator and denominator by the numerator; then we have

$$\frac{\boldsymbol{N}}{N_0}\eta = \frac{\sigma_1}{(1/\mu) + a + b\mu + c\mu^2 + \ldots} \quad \ldots\ldots\ldots \quad (29)$$

where $a = \sigma_1 - 2\sigma_2$, $b = \sigma_2(4\sigma_2 - 3\sigma_3 - \sigma_1)$, and $c = 2\sigma_2(6\sigma_2\sigma_3 - 2\sigma_3\sigma_4 + \sigma_1\sigma_2 - \sigma_1\sigma_3 - 4\sigma_2^2)$. Now (quoting Langmuir), " if σ_1 and σ_2 are different, but all subsequent values of σ are equal to σ_2, then all coefficients in (29) above b are zero." By making this assumption, which is essentially the same as Brunauer's, it is seen that

$$\frac{\boldsymbol{N}}{N_0}\eta = \frac{\sigma_1\mu}{1 + \sigma_1\mu - 2\sigma_2\mu + \sigma_2^2\mu^2 - \sigma_1\sigma_2\mu^2} \quad \ldots\ldots\ldots \quad (30)$$

Equation (30) factorises readily into

$$\frac{\boldsymbol{N}}{N_0}\eta = \frac{\sigma_1\mu}{(1 - \sigma_2\mu)[1 + (\sigma_1 - \sigma_2)\mu]} = \frac{1}{1 - \sigma_2\mu} - \frac{1}{1 + (\sigma_1 - \sigma_2)\mu} \quad \ldots \quad (31)$$

$\eta\boldsymbol{N}/N_0$ is equivalent to the V/V_m of Brunauer; it is the total adsorption expressed as the number of monolayers.

If one uses the nomenclature of Brunauer and follows the Langmuir method, an expression comparable to (26) is obtained and, after making the Langmuir–Brunauer assumption and dividing algebraically the numerator into the denominator, one obtains the expression (32)

$$\frac{V}{V_m} = \frac{y}{(1 - x)[1 - (x - y)]} = \frac{1}{1 - x} - \frac{1}{1 - (x - y)} \quad \ldots\ldots \quad (32)$$

Comparing equations (32) and (31) it is clear that $y = \sigma_1\mu$, and x or $p/p_0 = \sigma_2\mu$. Brunauer's $c = y/x =$ Langmuir's σ_1/σ_2 or the ratio of the relative lives of the first and subsequent layers. Substituting cx for y in equation (32) we have the Brunauer equation for adsorption on a free surface, *i.e.*,

$$\frac{V}{V_m} = \frac{cx}{(1 - x)[1 - x(1 - c)]} \quad \text{(Brunauer, } \textit{op. cit.}\text{, p. 153).}$$

It should be stated here that Langmuir was of the opinion then that Case VI was operative when (1) the vapour being nearly saturated, the rate of evaporation from the second layer of molecules is comparable with the rate of condensation, and (2) the forces acting between the first and second layers of adsorbed molecules are greater than those holding the first layer to the surface. Langmuir's examination of equation (29) was limited to the statement that " at very low pressures η is proportional to μ but at pressures close to saturation η begins to increase rapidly and becomes infinite when saturation is reached."

It may be of interest to make some additional analysis of these equations. In general for all ratios of σ_1/σ_2, $\eta\boldsymbol{N}/N_0 = 0$ when $\mu = 0$, and $\eta\boldsymbol{N}/N_0 = \infty$ when $\mu = 1/\sigma_2$ or $1/(\sigma_2 - \sigma_1)$. The gradient at any point is given by the expression

$$\frac{\boldsymbol{N}}{N_0}\frac{\mathrm{d}\eta}{\mathrm{d}\mu} = \frac{\sigma_2}{(1 - \sigma_2\mu)^2} - \frac{\sigma_2 - \sigma_1}{[1 - (\sigma_2 - \sigma_1)\mu]^2} \quad \ldots\ldots\ldots \quad (33)$$

and as μ approaches 0, this expression approaches σ_1, or the initial slope at the origin of the adsorption curves ($\eta\boldsymbol{N}/N_0$ plotted against $\mu\sigma_2[\mu/\mu_{\text{sat.}}]$), is σ_1/σ_2, or on Brunauer's nomenclature, is c (V/V_m plotted against p/p_0). Further

$$\frac{\boldsymbol{N}}{N_0}\frac{\mathrm{d}^2\eta}{\mathrm{d}\mu^2} = \frac{2\sigma_2^2}{(1 - \sigma_2\mu)^3} - \frac{2(\sigma_2 - \sigma_1)^2}{[1 - (\sigma_2 - \sigma_1)\mu]^3}$$

and a point of inflection occurs when

$$\mu = \frac{1 - \left(\dfrac{\sigma_2 - \sigma_1}{\sigma_2}\right)^{\frac{2}{3}}}{\sigma_2 - \sigma_1 - \sigma_2\left(\dfrac{\sigma_2 - \sigma_1}{\sigma_2}\right)^{\frac{2}{3}}}$$

or, on Brunauer's nomenclature, when

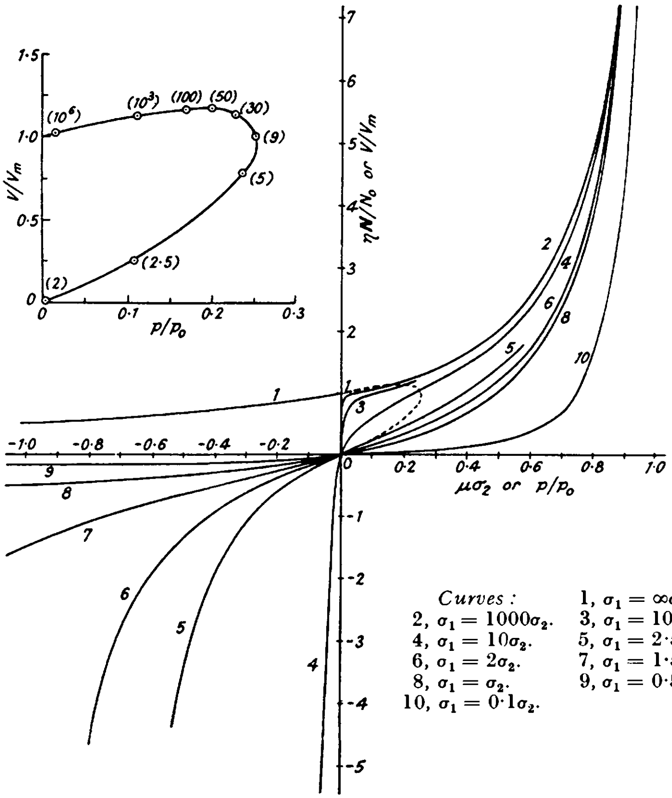
$$\frac{p}{p_0} = \frac{(c - 1)^{\frac{2}{3}} - 1}{(c - 1) + (c - 1)^{\frac{2}{3}}}$$

(*a*) If $\sigma_1 > \sigma_2$:

(1) $\sigma_1 > 2\sigma_2$: the point of inflection occurs at *positive* values of $\mu\sigma_2$ and $\eta N/N_0$, the theoretical isotherms being concave to $\mu\sigma_2$ from the origin to the inflection point. This case represents Brunauer's type II, when a sigmoid curve is found experimentally.

(2) $\sigma_1 = 2\sigma_2$: the point of inflection occurs at the origin. In Fig. 1 are arranged typical isotherms calculated for varying ratios of σ_1/σ_2, and the locus of the inflection points is marked as a broken line (see also Fig. 2). It extends from the origin when $\sigma_1/\sigma_2 = 2$, reaches a maximum in respect to μ for $\sigma_1/\sigma_2 = 9$ and then, passing through a maximum in respect to $\eta N/N_0$, returns to a value of $\eta N/N_0 = 1$ and $\mu = 0$ when $\sigma_1/\sigma_2 = \infty$ ($\sigma_2 \neq 0$).

FIG. 2. FIG. 1.



Point B. This is the point on the isotherm where the middle, flatter portion of the curve begins, and has been used to give the value of V_m. (V_m can also be calculated from the B.E.T. equation.) It is clearly the beginning of the " inflection period," where the previously rapid change of gradient is approaching the point where $\frac{N}{N_0}\frac{d^2\eta}{d\mu^2} = 0$. It may be a help in the fixing of point B to know the theoretical inflection point (σ_1/σ_2 or c being known). It would appear from the curves in Fig. 1, that the tendency would be to fix a value of V greater than the real value of V_m if c is greater than 10. Actually if $c = 9$, $\mu\sigma_2 = 0{\cdot}25$ and $\eta N/N_0 = 1$, so that the inflection point itself gives the correct monolayer value. If $c > 9$, $\eta N/N_0$ has values at the inflection point a little greater (up to 16%) than the correct monolayer value ; almost the correct value is given again as c gets very large. If $c < 9$, the inflection point values rapidly fall below the monolayer value for $\eta N/N_0$. Theoretically, therefore, and for adsorbents on a free surface, the locus of the inflection points might prove a useful guide in determining which point on the experimental curve gives the best approximation to $V = V_m$; it is clearly not in general " the beginning of the flat portion of the curve." (It may be of value in this connection to investigate, as above, the shape of the theoretical curves when $n \neq \infty$. For certain values of n and c two points of inflection would be found, the first being near the value of $\eta\boldsymbol{N}/N_0$ for $n = \infty$, and the above discussion might be of value in this case also in helping to fix the point where $\eta\boldsymbol{N}/N_0 = 1$.)

It is seen from the curves that when σ_1/σ_2 has values close to but greater than 2, the point of inflection approaches the origin, *e.g.*, curve 5 where $\sigma_1/\sigma_2 = 2{\cdot}5$, and it is difficult to detect the sigmoid type in the *experimental* curve where, of course, the part of the curve when η and μ have negative values is not available as it is in the *theoretical* isotherms of Fig. 1. The explanation of this difficulty is that when σ_1/σ_2 approaches ∞, the initial gradient approaches ∞ and the gradient at the point of inflection approaches 1; as σ_1/σ_2 decreases, so does the initial gradient (σ_1/σ_2), but the gradient at the point of inflection increases until the two gradients become identical and equal to 2 when $\sigma_1/\sigma_2 = 2$ and the point of inflection is at the origin.

The Type II curves of Brunauer are found then when σ_1/σ_2, or c, exceeds 2; the limiting conditions are (1) when $\sigma_1/\sigma_2 = \infty$ $(\sigma_2 \neq 0)$ and (2) when $\sigma_1/\sigma_2 = 2$.

According to Brunauer's approximation that in the expression $c = \dfrac{a_1}{b_1} \cdot \dfrac{b_2}{a_2} \cdot e^{(E_1 - E_L)/\boldsymbol{R}T}$, a_1b_2 can be taken without much error as equal to a_2b_1, c becomes $e^{(E_1 - E_L)/\boldsymbol{R}T}$. It is seen that the Type II curve changes over to the Type III, not as usually stated when $E_1 = E_L$ but when $e^{E_1/\boldsymbol{R}T} = 2e^{E_L/\boldsymbol{R}T}$ or, if $T = 300°$, when $E_1 = E_L + 420$ cals. approx.

The case when σ_1/σ_2 has become ∞ $(\sigma_2 \neq 0)$ is interesting. From equation (31) it is seen that in the limit in this case $\eta\boldsymbol{N}/N_0 = 1/(1 - \sigma_2\mu)$. This is a hyperbola with asymptotes $\eta\boldsymbol{N}/N_0 = 0$ and $\mu = 1/\sigma_2$.* For positive values of $\eta\boldsymbol{N}/N_0$ the curve follows closely curve 2 in Fig. 1 from infinity, when $\mu = 1/\sigma_2$, and crosses the ordinate at $\eta\boldsymbol{N}/N_0 = 1$; its continuation for negative values of $\mu\sigma_2$ is shown in Fig. 1. This curve represents the further adsorption, according to this model, on an initially complete monolayer.

It will be noted in the theoretical curves of Fig. 1, as is evident from actual adsorption isotherms given in Brunauer's book (*op. cit.*), that for values of μ in the range $0{\cdot}7/\sigma_2$ $(\equiv 0{\cdot}7\ p/p_0)$ upwards, the isotherms would be difficult to detect separately in practice for values of $c > 10$. It should be possible theoretically to determine V_m for such cases, by fitting an experimental curve against this calculated curve for V/V_m against p/p_0 where c is ∞. The calculated curve $(c = \infty)$ would leave the experimental curve at some value of p/p_0, and where it crosses the ordinate would give the value of V which is equal to V_m.

Preliminary calculations show that similar procedures could be used where the adsorption is not on a free surface but where the isotherm is represented by the Brunauer equation (*op. cit.*, p. 154) where n = the number of adsorbed layers that could be fitted into the idealised capillary tube system of an adsorbent.

Another way of making use of this coincidence of the curves at high values of p/p_0 in order to obtain a value for V_m may be illustrated by an example; the theoretical value of V/V_m for $c = \infty$ at a value of p/p_0 of $0{\cdot}9$ is 10; the value of V/V_m that would be observed at the same value of p/p_0 if the experimental curve had a value of $c = 10$ would be $9{\cdot}9$; the value of V_m so calculated from a single adsorption point would thus be 1% low. The error involved in this calculation depends on the value of c.

(*b*) If $1 < \sigma_1/\sigma_2 < 2$: The curves retain their point of inflection, which however now occurs at negative values of $\eta\boldsymbol{N}/N_0$ and μ; $\eta\boldsymbol{N}/N_0$ as before becomes ∞ at the values of $\mu = 1/\sigma_2$ and $1/(\sigma_2 - \sigma_1)$; *e.g.*, if $\sigma_1 = 1{\cdot}5\sigma_2$, the point of inflection is at $-0{\cdot}327/\sigma_2$ and the curve passes to infinity at $\mu = +1/\sigma_2$ and at $-2/\sigma_2$. As regards the *realisable* part of the adsorption curve this case belongs to the Brunauer Type III.

(*c*) If $\sigma_1 = \sigma_2$: Equation (31) becomes

$$\frac{\boldsymbol{N}}{N_0}\eta = \frac{\sigma_2(\sigma_1)\mu}{1 - \sigma_2(\sigma_1)\mu}$$

This again is a hyperbola with asymptotes at $\eta\boldsymbol{N}/N_0 = -1$ and $\mu = 1/\sigma_2$ (see curve 8). This represents a limit to the *theoretical* sigmoid curve of Type II, the other limit being the hyperbola obtained when $\sigma_1/\sigma_2 = \infty$. These two hyperbolæ, which represent the limiting cases for theoretical sigmoid adsorption curves on this model, have the same gradients throughout $\dfrac{\boldsymbol{N}}{N_0}\dfrac{d\eta}{d\mu} = \dfrac{\sigma_2}{(1 - \sigma_2\mu)^2}$, and are convex to the abscissa, as an inspection of the second differential shows. Indeed they represent similar adsorption processes: one is the multilayer formation on a completed monolayer whose adsorptive properties are assumed to be equivalent to those

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* See also Gregg and Jacobs, *Trans. Faraday Soc.*, 1948, **44**, 577.

of the liquid at the same temperature ($\sigma_2 = \sigma_3 \ldots\ldots \sigma_L$) and the other is the multilayer formation occurring on a surface whose adsorptive properties are equivalent to those of the liquid ($\sigma_1 = \sigma_2$). As has already been pointed out, the *realisable* sigmoid adsorption isotherms have their limit at $\sigma_1 = 2\sigma_2$, when the inflection point has reached the origin. This case (*c*) also belongs to Type III of Brunauer's classification.

It is interesting to compare these cases with the Langmuir Case I (so-called Langmuir adsorption equation), $\dfrac{\boldsymbol{N}}{N_0}\eta = \dfrac{\sigma_1\mu}{1 + \sigma_1\mu}$. ($\sigma_2 = 0$), which is, of course, also a hyperbola with asymptotes $\eta\boldsymbol{N}/N_0 = 1$ and $\mu = -1/\sigma_1$. This curve is concave to the abscissa for positive values of μ $\left(\dfrac{\boldsymbol{N}}{N_0}\dfrac{d^2\eta}{d\mu^2} = \dfrac{-2\sigma_1^2}{(1 + \sigma_1\mu)^3}\right)$. The initial slope ($\mu = 0$) is σ_1 and a monolayer is adsorbed only when $\mu(p) = \infty$; at saturation, ($\mu_{sat.}$ or p_0), the fraction of a monolayer adsorbed is determined by the values of σ_1 and $\mu_{sat.}$ and may be quite small for non-volatile liquids with small values of σ_1. Since $\mu_{sat.}$ is equal to $1/\sigma_2$, this monolayer fraction is determined by the ratio σ_1/σ_L. If the adsorbing surface is of such a kind that $\sigma_1 = \sigma_L$ then at saturation $\eta\boldsymbol{N}/N_0 = 1/2$, as would be the case also for adsorption on the liquid surface itself [the adsorption process is assumed to be limited to a monolayer which is reached (theoretically) at $\mu = \infty$].

(*d*) $\sigma_1 < \sigma_2$ or $0 < c < 1$; *e.g.*, curve 10 when $\sigma_1 = 0{\cdot}1\sigma_2$: Dealing first with the *realisable* portion of the curve, we see that the adsorption is small until considerable values of $\mu\sigma_2$ are reached and that then a steep increase in $\eta\boldsymbol{N}/N_0$ occurs as the curve approaches $\mu = 1/\sigma_2$. Theoretically, after passing through the origin, all curves show a minimum at $p = -p_0/\sqrt{(1 - c)}$ and a point of inflection as the curve becomes asymptotic to $\eta\boldsymbol{N}/N_0 = 0$. Beyond the saturation value other, theoretical, portions of the curve occur, with, for example, a maximum appearing at $p = +p_0/\sqrt{(1 - c)}$. The *realisable* portion of the isotherm, however, is again of Type III, which therefore is found ranging from $\sigma_1/\sigma_2 = 2$ to $\sigma_1/\sigma_2 =$ a very small value, or when $E_1 = E_L + 420$ cals. (approx.) at room temperature, to $E_1 < E_L$, $E_1 \neq 0$, the previous assumptions holding.

The resemblance between Langmuir's Case VI and the B.E.T. equation for adsorption on a free surface has been pointed out and it has been recalled that the same basic equation holds also for Langmuir's Case IV. Brunauer and his co-workers have made an interesting extension of their theory to cover the case where the adsorption may be limited by the width of the capillary spaces in the adsorbents. The equation covering this case is derived by summing the infinite series in the numerator and denominator of equation (26) to a finite number of terms, the same assumptions being made as before. Both series are of well-known form and can readily be summed to n terms or to infinity. It is clear therefore, and perhaps worth recording, that the same equation is thus obtained as in Langmuir's Case IV where n is the number of molecules per elementary space. The assumption that the relative lives of the adsorbed molecules can be considered equal if $n > 2$ is, perhaps, less plausible here than in the former case. However, this general similarity may partly account for the ability of the Brunauer equation to fit experimental results when the adsorption is a monolayer or less at high values of p/p_0, *e.g.*, the adsorption of iodine on silica gel (Brunauer, *op. cit.*, p. 165). It is intended to make a further analysis of this case later and attention is directed here only to some very general considerations concerning it.

As already pointed out, when $n = \infty$ and for values of $c > 10$ (say), the first layer is almost completed at fairly low values of p/p_0 and, therefore, the parts of the isotherm where p/p_0 have high values are difficult to distinguish; these parts of the isotherm are almost independent of c. This occurs also when n is finite; the value of V/V_m at saturation, now finite, is little affected by the value of c, if $c > 10$. This insensitiveness to the value of c at saturation is diminished by a greater value of n; *e.g.*, if $n = 2$, V/V_m at saturation $= (3/2)(20/21)$ for $c = 10$, $(3/2)(200/201)$ for $c = 100$, and $3/2$ for $c = \infty$; if $n = 6$, the corresponding values are $(7/2)(60/61)$, $(7/2)(600/601)$, and $7/2$. In general, for any values of n, $V/V_m = 0$ when $p/p_0 = 0$, $V/V_m = n$ when $p/p_0 = \infty$, the initial gradient $= c$ and when $p/p_0 = 1$, $V/V_m = [c\eta/(1 + c\eta)][(\eta + 1)/2]$; this expression approaches $(n + 1)/2$ as c approaches ∞ .

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