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any interest. The setting of a given H_{ij} in the potentiometric computer, which involves merely adjusting a potentiometer, is much simpler than connecting together several standardized condensers or coils as in the network analyzer.

The potentiometric secular equation computer can also solve non-homogeneous linear equations by setting the E and $1/E$ potentiometers at

unity, using H_{ij} 's to represent positive matrix components and D_{ij} 's to represent negative matrix components, and keeping one C_i at unity, the corresponding H 's and D 's representing the constant terms in the equations.

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Multilayer Gas Adsorption on Composite Surfaces

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(February 19, 1947)

The equation of Brunauer, Emmett, and Teller (BET) for the adsorption of a gas on a free plane homogeneous surface is extended to the case of a mixture of two such surfaces, in an attempt to explain the observed deviations below one monolayer. The resulting equation may be greatly simplified for the case that the adsorption energy parameter, c , for each component surface, is large with respect to unity, as is usually the case in low temperature adsorptions of nitrogen, argon, etc. This approximate form of the equation is applied to the nitrogen isotherm on an inorganic salt and gives substantially better agreement

with experiment than does the simple BET equation. The region of agreement between the experimental and BET isotherms is discussed on the basis of a two-component surface, and conditions are given under which one might obtain *two* distinct regions of the isotherm which are fitted by the BET equation by the use of two sets of parameters. It is suggested that it is the lower of these two regions which gives rise to the occasionally observed "saturation adsorption" values corresponding to only small fractions of a monolayer.

INTRODUCTION

FOR gas adsorption in the range below about 0.8 monolayer it is commonly observed that the theoretical isotherm of Brunauer, Emmett, and Teller^{1,2} (BET) for a free plane homogeneous surface, based on the rectilinear plot fitting best in the neighborhood of one monolayer, predicts too low an adsorption. A typical example of this behavior is shown in Fig. 1 for the nitrogen adsorption isotherm at 78°K on an inorganic salt; Fig. 2 gives the corresponding rectilinear plot. The departure from the theoretical curve is usually attributed³ to an inhomogeneity of the

surface, which leads to preferential adsorption on those areas which have high energies of adsorption, and which therefore justly belong to higher values of the energy parameter,⁴ c , than that given by the best fit near one monolayer—i.e., on the more "uniform" part of the surface. Most calorimetric data^{3,5} for adsorptions below one monolayer lend support to this interpretation, as do also the abnormally large c values obtained, for example, by Armbruster⁶ and co-workers at very low relative pressures in the low temperature adsorption of inert gases on metals.

If surface inhomogeneity is indeed responsible for these low adsorption discrepancies, it poses an

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

² An excellent review of the theory is contained in Brunauer's book, *The Adsorption of Gases and Vapors*, Vol. I, *Physical Adsorption* (Princeton University Press, Princeton, 1943), p. 151 *et seq.*

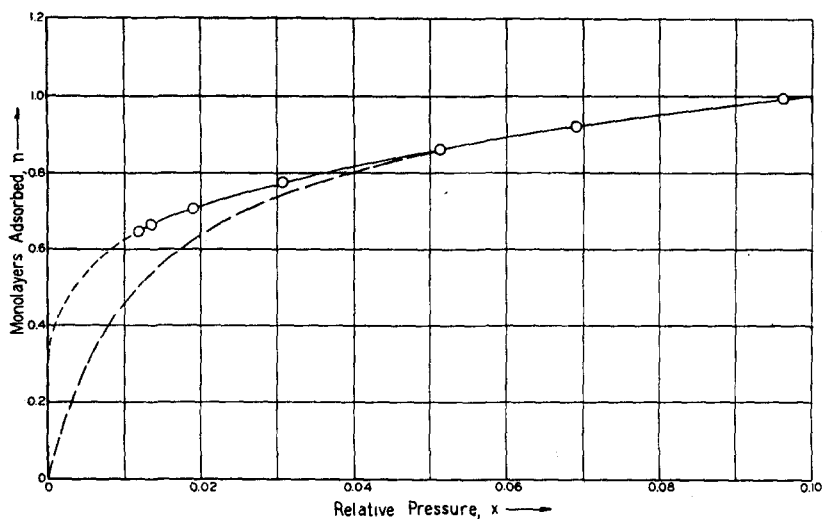
³ Reference 2, pp. 158, 335.

⁴ The energy parameter, c , is given by Brunauer, Emmett, and Teller as $c = \exp(E_1 - E_L)/RT$, where E_1 and E_L are, respectively, the energy of adsorption into the first layer and the energy of liquefaction.

⁵ See, for example, W. D. Harkins and G. E. Boyd, J. Am. Chem. Soc. **64**, 1145 (1942); W. D. Harkins and G. Jura *ibid.* **66**, 919 (1944), Fig. 8.

⁶ M. H. Armbruster, J. Am. Chem. Soc. **64**, 2545 (1942); M. H. Armbruster and J. B. Austin, *ibid.* **66**, 159 (1944).

FIG. 1. Comparison between experimental (solid line) and theoretical BET (dashed line) isotherms in the low relative-pressure region in the adsorption of nitrogen on an inorganic salt. (For data see Table I.) The abscissa letter "n" should be replaced by "p."



interesting question as to why the BET equation, derived on the assumption of uniformity of surface, fits the data even approximately. However, with inhomogeneous surfaces being the general rule, it is not surprising that for such definitely non-uniform substrates as promoted catalysts the BET plots are, by and large, rectilinear over as wide a range as for samples of high purity.

By directing attention to the discrepancies in the low relative pressure range there is no intention of minimizing the importance of those existing at higher pressures, which are generally larger in absolute magnitude though of the same order percentually. However, attempts to improve the theory in the higher range encounter difficulties which are probably unimportant at low relative pressures by virtue of the fact that here there is little multilayer adsorption, and the theoretical result is relatively independent of any inaccuracies⁷ in the model of the adsorbed phase for large adsorptions. It thus appears fruitful to examine the low pressure discrepancies in the light of a somewhat generalized BET theory obtained without making any fundamental changes in the assumed mechanism of the adsorption process.

The rather evident generalization to be proposed, then, is to take account of the surface inhomogeneity, as specified by several sets of the surface parameters c_i , v_{mi} , and θ_i , where the first

two have their usual meanings^{4,8} and θ_i is the fraction of the total sample surface which is of type i :

$$\theta_i = v_{mi} / \sum v_{mj}, \quad \sum \theta_i = 1.$$

In itself, the assumption of surface inhomogeneity is not new, having been suggested originally by Langmuir⁹ and applied to the Langmuir equation by Zeldowitsh,¹⁰ who obtained the Freundlich isotherm in this way on the basis of a rather special distribution of the heat of adsorption over the surface. In the present treatment it will be assumed that the BET theory is correct for a perfectly uniform surface, and the discussion will be limited to the case of unrestricted adsorption on plane surfaces.

THE GENERAL TWO-COMPONENT SURFACE

The simplest type of heterogeneous surface for our purpose can be imagined to consist of a mechanical mixture of two solid components, perhaps in finely-divided form, but such that the faces of the ultimate crystallites of each component are plane surfaces whose adsorptive properties do not vary radically among the various crystal forms present. (The particles should, of course, be large enough that edge effects may be neglected.) For such a two-component surface—

⁸ v_m is the volume of gas (usually at S.T.P.) which corresponds to a complete closely packed monolayer.

⁹ I. Langmuir, *J. Am. Chem. Soc.* **40**, 1371 (1918); cf. reference 2, pp. 77ff.

¹⁰ J. Zeldowitsh, *Acta Physicochimica (URSS)* **1**, 961 (1934).

⁷ Cf. T. L. Hill, *J. Chem. Phys.* **14**, 263 (1946).

which we shall call "composite"—the BET theory predicts a total adsorption, v , given by the sum of terms of the usual type:

$$v = \frac{xv_m}{1-x} \left\{ \frac{\theta_1 c_1}{1+(c_1-1)x} + \frac{\theta_2 c_2}{1+(c_2-1)x} \right\}, \quad (1)$$

wherein $v_m = v_{m1} + v_{m2} = \theta_1 v_m + \theta_2 v_m$, and x is the relative pressure, obtained by dividing the equilibrium adsorption pressure by the vapor pressure of the liquefied adsorbate. The usual BET equation,

$$v = \frac{xv_m}{1-x} \left\{ \frac{c}{1+(c-1)x} \right\}, \quad (2)$$

determines the two surface parameters v_m and c from the region of linearity of the rectifying plot (cf. Fig. 2). Since for a given adsorbate v_m is essentially a geometric property of the surface, the value so obtained will be assumed to be

$$\frac{xv_m}{v(1-x)} = \left[\frac{c(x)-1}{c(x)} \right] x + \frac{1}{c(x)} \quad (3)$$

$$= \left[\theta_1 \left(\frac{c_1}{c_1-1} \right) + \theta_2 \left(\frac{c_2}{c_2-1} \right) \right]^{-1} x + \frac{1}{c_0} \left\{ 1 + \frac{\theta_1 \theta_2 c_0 \left(\frac{1}{c_2} - \frac{1}{c_1} \right)^2 \left[\theta_1 \left(\frac{c_2-1}{c_2} \right) + \theta_2 \left(\frac{c_1-1}{c_1} \right) \right]^{-3}}{x + \frac{c_0}{c_1 c_2} \left[\theta_1 \left(\frac{c_2-1}{c_2} \right) + \theta_2 \left(\frac{c_1-1}{c_1} \right) \right]^{-1}} \right\}^{-1}, \quad (4)$$

where

$$c_0 = \frac{\left[\theta_1 \left(\frac{c_1}{c_1-1} \right) + \theta_2 \left(\frac{c_2}{c_2-1} \right) \right]^2}{\frac{\theta_1}{c_1} \left(\frac{c_1}{c_1-1} \right)^2 + \frac{\theta_2}{c_2} \left(\frac{c_2}{c_2-1} \right)^2}. \quad (5)$$

Equation (4) follows exactly from Eq. (1) and is written in this form to display its similarity to Eq. (3). On equating the right sides of Eqs. (3) and (4) it will be possible to cancel the two terms linear in x for large values of $c(x)$, c_1 , and c_2 , where unity is negligible, and thereby obtain

$$c(x) = c_0 \left[1 + \frac{\theta_1 \theta_2 c_0 (1/c_2 - 1/c_1)^2}{x + c_0/c_1 c_2} \right], \quad (6)$$

¹¹ We shall find no theoretical upper x -limit to the fit, since the BET theory has been assumed exact for each individual component at all x , and the surface heterogeneity introduces deviations only at small x ; cf. Eq. (6).

correct, and is the one to be used in Eq. (1). Experimental deviations from Eq. (2) are thus attributed entirely to the inconstancy of c . If we substitute in Eq. (2) an isotherm relation of the form $v=f(x)$, c is implicitly defined as a function of x and will be written $c(x)$ to distinguish it from the BET c constant obtained from the rectifying plot. The plan will be to use Eq. (1) for the function $f(x)$ and to compare the behavior of the resulting function $c(x)$ with that obtained by employing the experimental isotherm for $f(x)$. This procedure is more convenient than a direct comparison of Eq. (1) with the experimental isotherm, since it gives a second-order correction to the first approximation, i.e., the BET equation, and will clearly show how $c(x)$ may be constant over a range¹¹ of x .

By inverting and rearranging Eqs. (1) and (2) we obtain:

where the same approximation gives

$$c_0 = (\theta_1/c_1 + \theta_2/c_2)^{-1}. \quad (7)^{12}$$

In this connection it is noteworthy that for low temperature adsorptions of nitrogen, argon, carbon monoxide, etc., BET c constants much below 50 are seldom observed.

With the restriction to large c -values, both the expressions $\theta_1 \theta_2 c_0 (1/c_2 - 1/c_1)^2$ and $c_0/c_1 c_2$ will be of the order of 10^{-2} or less. It may thus be seen qualitatively from Fig. 1 that Eq. (6) furnishes the correct type of behavior for $c(x)$ as calculated from Eq. (2), using the lower portion of the experimental isotherm: at large x (~ 0.2), $c(x)$ is essentially a constant, c_0 , and

¹² This expression is easily generalized to a larger number of component surfaces by considering the first pair as one component, then adding a third, and so on; thus,

$$\frac{1}{c'} = \left(\frac{\theta_0}{c_0} + \frac{\theta_3}{c_3} \right) = \left[\theta_0 \left(\frac{\theta_1}{c_1} + \frac{\theta_2}{c_2} \right) + \frac{\theta_3}{c_3} \right] = \left(\frac{\theta_1'}{c_1} + \frac{\theta_2'}{c_2} + \frac{\theta_3'}{c_3} \right).$$

increases with decreasing x , corresponding to the increasing difference between the theoretical and experimental curves. The linearity of Eq. (4) and the constancy of $c(x)$ thus depend upon the value of the second term in brackets in Eq. (6). If c_1 and c_2 are both very high, this term is negligible with respect to unity and $c(x)$ becomes essentially c_0 .

A conclusion which seems somewhat odd at first sight is that for given values of θ_2 and c_2 , the larger the value of c_1 , the less it affects the value of c_0 as given by Eq. (7). The reason for this is that for large c_1 , the adsorption on this part of the surface (hereafter called "surface 1") is essentially complete at a very low value of x , so that the graphically-determined c constant deals only with changes in the adsorption on surface 2 and in the second and higher layers of surface 1 (which by hypothesis have the c constant unity).

The most interesting applications of these results arise when $c_1 \gg c_2$ (or *vice versa*), since if they are nearly equal Eq. (1) reduces to Eq. (2) almost identically. With this inequality, which will be assumed throughout the rest of the paper, we have from Eq. (7)

$$c_0 \approx c_2/\theta_2, \quad (8)$$

provided θ_2 is not much less than θ_1 . A further result is that for values of $x \gg c_0/c_1 c_2$ we would expect the quantity $[c(x)/c_0 - 1]x$ from Eq. (6) to be nearly constant. Then with the help of Eq. (8) we have

$$c_0[c(x)/c_0 - 1]x \approx \theta_1/\theta_2, \quad (9)$$

which permits the experimental evaluation of θ_1 and θ_2 . Here $c(x)$ is to be obtained by substitution of the experimental isotherm into Eq. (2), as described earlier, and c_0 is essentially the BET c constant. Actually we later note a small difference between c_0 and c and also use an indirect method for calculating $[c(x)/c_0 - 1]x$.

THE LOWER LIMIT OF FIT OF THE BET EQUATION

Before turning to the experimental comparison it is perhaps appropriate to investigate the lower limit of fit of the BET equation for the case just considered. Emmett¹³ has often emphasized the usefulness of the rule-of-thumb that, for low

¹³ P. H. Emmett, J. Am. Chem. Soc. **68**, 1784 (1946); see also reference 2, p. 336.

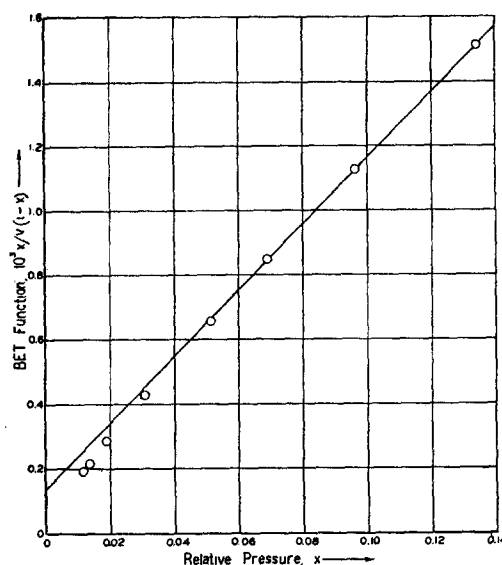


FIG. 2. BET rectilinear plot for nitrogen adsorption at 78°K on an inorganic salt. (For data see Table II.)

temperature adsorptions at least, the region of agreement is generally about $0.05 \leq x \leq 0.35$.¹¹ Intuitively, however, it would seem that these limits should be specified rather in terms of the number, $\nu = v/v_m$, of adsorbed layers, since this quantity is more directly related to the state of the adsorbed phase than is the relative pressure. In fact it is easily seen from Eq. (9) that the fractional deviation of $c(x)$ from c_0 is a function of the product $(c_0 x)$ rather than of x alone; we wish now to find its dependence on the amount adsorbed.

In order that Eq. (2) hold in a given range, it is necessary that throughout that range c be constant within some specified allowable deviation. To determine the order of magnitude of this variation, it must be translated into the variation in ν . For this purpose, the derivative of Eq. (2) gives the relation

$$d \ln \nu = [1 - \nu(1-x)] d \ln c. \quad (10)$$

(Although we specifically permit small variations in c , it will not differ appreciably from the BET c constant and will be so treated in these order-of-magnitude calculations.) The quantity $\nu(1-x)$ is the fraction of the layer adjacent to the substrate which is completed (not to be confused with "the fraction of the surface covered by exactly one layer"). In other words, the quantity

TABLE I. Comparison of theory with experiment: the isotherm.

I p (mm) ^a	II x^a	III v_{ads} (cc. STP)	IV v_e (exp) ^b	V v (BET)	VI $10^3x \cdot$ $[c(x)/c_0 - 1]^b$	VII v' (Eq. (23))
—	0.005	—	—	0.2912	—	0.5364
—	.01	—	—	.4552	—	.6104
9.1	.0118	61.58	0.6450	.5013	9.33†	.6320
10.4	.0135	63.34	.6634	.5330	9.54†	.6507
—	.015	—	(.687)	.5613	(10.39)	.6658
14.6	.0189	67.17	.7035	.6224	7.95†	.7008
—	.02	—	(.712)	.6364	(7.86)	.7098
—	.025	—	(.743)	.6929	(6.57)	.7462
—	.03	—	(.770)	.7373	(4.06)	.7666
23.6	.0306	73.87	.7737	.7431	5.06†	.7800
—	.04	—	(.817)	.8040	(3.00)	.8262
—	.05	—	(.856)	.8530	—	.8659
39.6	.0513	82.17	.8606	.8605	†Av. = 8.0	.8705
53.3	.0690	87.79	.9195	.9212	—	.9249
—	.075	—	(.934)	.9385	—	.9409
74.4	.0964	94.75	.9924	.9921	—	.9910
—	.1	—	(1.000)	1.0002	—	.9993
103.6	.1342	102.61	1.0747	1.0700	—	1.0670
—	.15	—	(1.100)	1.0997	—	1.0965
149.6	.1938	112.39	1.1772	1.1799	—	1.1764
—	.2	—	(1.189)	1.1913	—	1.1878

^a $p_0 = 772$ mm.^b Values in () obtained by interpolation.

$[1 - \nu(1 - x)]$ is the fraction of the total surface which is uncovered; or in the BET notation, s_0/A , where A is the total surface area and s_0 the area covered by exactly zero layers. That this follows directly from the BET relations,²

$$s_1 = c x s_0, \quad (11)$$

$$s_i = x s_{i-1} \quad (i > 1), \quad (12)$$

$$s_i = c x^i s_0 \quad (i \geq 1), \quad (13)$$

is shown by:

$$\begin{aligned} s_0/A &= s_0 / \sum_{i=0}^{\infty} s_i = s_0 / s_0 \left(1 + c \sum_{i=1}^{\infty} x^i \right) \\ &= (1 - x) / [1 + (c - 1)x] \\ &= 1 - \nu(1 - x). \end{aligned} \quad (14)$$

TABLE II. Comparison of theory with experiment: the BET rectifying plot.

x	$10^3x/v(1-x)$ Experimental	BET ^a
0.0118	0.194	0.251
.0135	.216	.269
.0189	.287	.325
.0306	.427	.446
.0513	.658	.659
.0690	.845	.843
.0964	1.126	1.126
.1342	1.511	1.517
.1938	2.139	2.133

^a Calculated from the least-squares line, Eq. 18, based on the last five experimental points of this table

For values of c , say in excess of 20, this quantity, $[1 - \nu(1 - x)]$, will be less than 0.2 for all $\nu > 0.85$, as is readily proved from Eqs. (11)–(13). Employing this result in Eq. (10), one sees that under these conditions a change of ± 10 percent in c is equivalent to ± 2 percent in ν , a reasonable figure for the agreement between theory and experiment. A variation in c outside this rather arbitrary permissible range of 20 percent will therefore determine the limit of fit.

We are now in a position to convert Eq. (6), or rather its approximate form, Eq. (9), into a form which depends primarily on the amount adsorbed. From Eq. (2) we have

$$(1/xc) = [\nu(1 - x)]^{-1} - 1. \quad (15)$$

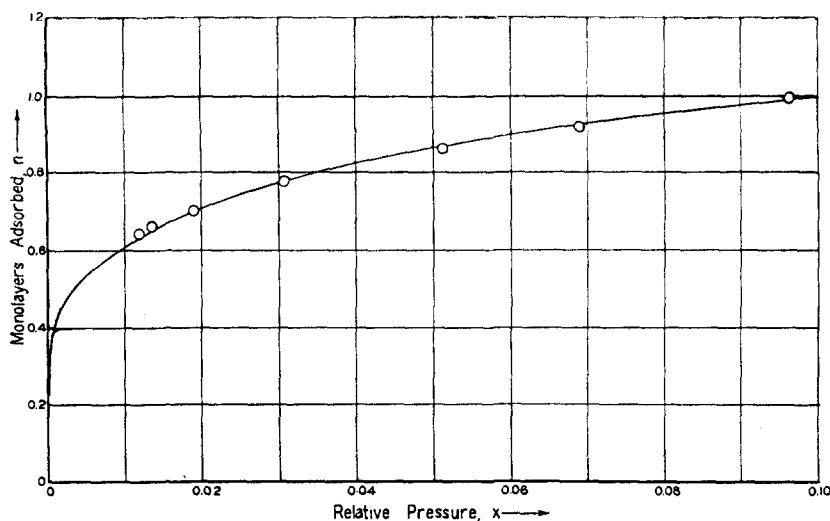
This is seen to be just the ratio of uncovered to covered surface and again, for reasonably high c values, is less than 0.25 for all $\nu > 0.85$. Since for the range in which we are interested $c \approx c_0$, use of Eq. (15) in (9) gives the fractional difference in $c(x)$ as

$$[c(x)/c_0 - 1] \approx \frac{\theta_1}{\theta_2} \left(\frac{1}{c_0 x} \right) \quad (16)$$

$$\approx \frac{\theta_1}{\theta_2} \{ [\nu(1 - x)]^{-1} - 1 \}. \quad (17)$$

Now Emmett's value for the lower limit of fit at $x = 0.05$ is obtained for samples with c (or c_0) ~ 100 . By Eq. (16) this would give a 20 percent deviation in $c(x)$ from c_0 if $\theta_1 \sim \theta_2$, and it is not unreasonable to expect that this latter condition might hold in a large fraction of the cases. If so, a large c constant implies a fit to very low values of x , and this has been the general rule in the experience of the writer. (Of course, we assume all along that $c_1 \gg c_2$.) By Eq. (17), under the same condition that $\theta_1 \sim \theta_2$, the lower limit of fit corresponding to a 20 percent deviation in $c(x)$ would be at about 0.9 monolayer. These figures are, of course, very dependent upon the ratio θ_1/θ_2 , and it appears possible on the basis of the equations to obtain agreement with experiment to very low x , or low adsorptions, regardless of the magnitude of c , if the surface is highly uniform. Indications are, however, that such surfaces are most exceptional.

FIG. 3. Comparison between experimental points and theoretical isotherm (full line) based on extension of the BET theory to a two component surface. (For data see Table I.) The abscissa letter "n" should be replaced by " ν ."



APPLICATION TO AN EXPERIMENTAL ISOTHERM

The data plotted in Figs. 1 and 2 are given in the first five columns of Table 1. The least-squares line, namely,

$$x/\nu(1-x) = 10^{-2}(1.035x + 0.0129), \quad (18)$$

through the last five points of Table II gives the BET constants: $\nu_m = 95.47$, $c = 81.2$. These have been employed in calculating the number of adsorbed layers experimentally observed (ν_e) and predicted by the BET theory (ν), listed respectively in columns IV and V of Table I. The last column contains the isotherm figures calculated on the basis of the two-component surface, as will be described presently.

The quantity $[c(x)/c_0 - 1]x$ of Eq. (9), tabulated in column VI, was calculated from the relation

$$[c(x)/c_0 - 1]x = \left(\frac{1}{\nu} - \frac{1}{\nu_e} \right) x / \left(\frac{1}{\nu_e} - 1 + x \right). \quad (19)$$

This is derived from the two equations obtained from Eq. (2) on replacing c and ν ($=\nu/\nu_m$) first by c_0 and ν (the BET ν), and then by $c(x)$ and ν_e , and evidently involves the assumption that c_0 equals the BET c constant. While this is by no means exact (*v.i.*), it is sufficient for calculating in first approximation the difference between c and c_0 . For greater accuracy one can use the value of c_0 , so obtained, to calculate a more exact difference, and so on, although the rapid convergence of this process and the crudeness of the

experimental data may not warrant the use of the higher approximations. The values obtained from Eq. (19) are evidently not very constant, since at low values of x the term (cf. Eq. (6)) c_0/c_1c_2 may be important, while at higher x values the small (and thus inaccurately estimated) difference between the experimental and BET curves introduces a large error; therefore, only those values were averaged which correspond to actual experimental points, the average being $[c(x)/c_0 - 1]x \approx 0.008$.

In order to obtain a better figure for c_0 we note that Eq. (9) now has the form

$$c(x) \approx c_0(1 + 0.008/x), \quad (20)$$

and hence the value of $c(x)$ exceeds c_0 by a quantity ranging from about 16 percent at $x=0.05$ to 4 percent at 0.2. Since the c constant ($=81.2$) obtained from the least-squares line, Eq. (18), is presumably an average of $c(x)$ over this range, a correction of about 10 percent must be applied to it to obtain c_0 ; this gives $c_0 = 73.2$. To go a step further, the average value 0.008 should now be corrected upward, since the actual value of c_0 is less than the c constant assumed for it in Eq. (19). In fact, if only c_0 is varied,

$$d \ln [c(x)/c_0 - 1]x = - \{ 1 + x/[c(x)/c_0 - 1]x \} d \ln c_0,$$

so that at $x \sim 0.015$ where the average was obtained, a change of -10 percent in c_0 causes a change of about $+25$ percent in $[c(x)/c_0 - 1]x$.

The average found is at best very approximate, but the θ 's are rather insensitive to it anyway; we shall therefore use the value

$$[c(x)/c_0 - 1]x \approx 0.01. \quad (21)$$

The third approximation to c_0 could now be made, but the correction is evidently quite small.

Employing the value of $c_0 = 73$ in Eq. (9) along with the average value given by Eq. (21), we obtain

$$\theta_1/\theta_2 \approx (0.01)(73)$$

or

$$\theta_2 \approx 0.6. \quad (22)$$

With this result one finds a fair fit to the experimental points using a c_1 of 50,000; however, this has a rather improbable shape at small x values, approaching the volume axis too rapidly. Trial and error shows that a much better fit is obtained by using $\theta_2 = 0.55$, which corresponds (cf. Eq. (9)) roughly to the highest values of column VI of Table I, and a c_1 of approximately 10,000. About c_1 we know only that it has to be much larger than c_2 to have a large effect on the shape of the isotherm in the low x region, since in the experimental example given—unfortunately the only one available at present—there are insufficient data in the low pressure region to fix c_1 accurately. Besides it is certainly an oversimplification to treat a randomly chosen surface as being composed of only two types, so we should probably not find an exact fit in any case.

The values of ν' found in the last column of Table I are therefore calculated according to the formula (cf. Eq. (1))

$$\nu' = \left(\frac{x}{1-x} \right) \left[\frac{(0.45)(10,000)}{1+10,000x} + \frac{(0.55)(40.2)}{1+39.2x} \right], \quad (23)$$

in which c_2 is obtained from Eq. (8) as $(0.55) \times (73.2) = 40.2$. The isotherm so obtained is plotted in Fig. 3, along with the experimental points. Comparison with Fig. 1 shows considerable improvement over the BET equation in the low pressure range.

It might be remarked in defense against the criticism that any equation which contains additional parameters *should* fit the data better than the simple BET theory, that Eq. (1) seems to be a logical first step in attempting to improve

the theory for low relative pressures, and that the parameters introduced turn out to have quite reasonable values in the light of the independent evidence mentioned in the introduction.

Without going into the subject of the disagreement between calorimetric heats of adsorption and those obtained from c , it should be noted that if the above example is typical and the interpretation correct, the heat of adsorption up to nearly half a monolayer should be larger than that appropriate to $c = 81$ by an amount $RT \ln(10000/81)$. At 78°K this is over 0.7 kcal./mole, a sizable fraction of the heat of liquefaction, 1.5 kcal./mole, of the nitrogen adsorbate. This correction is in the right direction to improve the agreement between the two methods, but is probably not the only difficulty^{13, 14} to be met.

THE CASE IN WHICH SURFACE 1 PREDOMINATES¹⁵

Another possible application of the equations for the two component surface is the case in which the adsorption on one part of the surface is negligibly small under the experimental conditions. With reference to Eq. (1) this will occur at such relative pressures that

$$\theta_1 c_1 / [1 + (c_1 - 1)x] \gg \theta_2 c_2 / [1 + (c_2 - 1)x]. \quad (24)$$

Besides the trivial case in which $\theta_2 \rightarrow 0$, resulting in Eq. (2) (which seldom occurs if the agreement of Eq. (2) with experiment throughout the range of 0–1.5 monolayers is a proper criterion), this may also happen when $\theta_2 \sim \theta_1$, provided $c_1 \gg c_2$ and x so restricted that $x \ll 1/c_2$. Evidence for this behavior should thus again be sought in the region below the usual range of fit of the BET theory.

A most interesting consequence of these conditions is that one is led to predict that Eq. (2) will apply in two distinct portions of the isotherm with two distinct sets of the parameters ν_m and c . One portion corresponds to the one just mentioned, in which the adsorption on surface 2 is a negligible fraction of the total; and the other corresponds to the case discussed in the previous section, wherein the adsorption in the first layer

¹⁴ A. B. D. Cassie, Trans. Faraday Soc. 282, 450 (1945).

¹⁵ Since Eq. (2) reduces to the Langmuir equation at $x \ll 1$, the results of this section are very similar to that given for the Langmuir equation; see reference 2, pp. 74, ff.

on surface 1 is essentially complete.¹⁶ Under these conditions the ratio of the v_m values found will be simply θ_1 , i.e. $v_{m1}/(v_{m1}+v_{m2})$.

Experimental results of this type have been frequently found, notably by Armbruster⁶ who obtained values of v_s , the Langmuir¹⁷ saturation adsorption (equivalent to $\theta_1 v_m$ or v_{m1} , if the present theory applies), corresponding to θ_1 values in the range 0.2–1 for argon, nitrogen, carbon monoxide, etc. on silver foil at 78 and 90°K, based on the assumption that v_m equals the apparent geometric area. While such figures are not unreasonable, this leaves unexplained the "coefficient of thermal expansion," $d \ln v_s / dT$, observed in that work. On the basis of the

¹⁶ Here we had best make again the restriction $c_2 \gg 1$, for otherwise c_0 will be low, and, correspondingly, the value of $x_m = 1/[1+(c)^2]$ so large that the usual deviations at large x may appear despite the approximate constancy of c as given by Eq. (6).

¹⁷ Reference 2, pp. 60, ff.

inhomogeneity hypothesis the temperature dependence of v_s would probably also be connected with the properties of surface 2, but a complete test of such an explanation must await measurements which extend throughout the range of about 0.05 to 1.5 monolayers (based on the largest v_m value obtained).

This extension of the BET equation appears to offer no explanation of the observed low roughness factors recently reported by Emmett,¹⁸ since these occur at relative pressures of 0.1 or above.

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¹⁸ Reported at the Chicago meeting of the American Chemical Society, September 1946; See Abstracts of Papers, 110th Meeting, No. 44, p. 25E.

Thermodynamics of Crystallization in High Polymers. I. Crystallization Induced by Stretching*

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A theory of oriented crystallization in elongated polymers having network structures (e.g., in vulcanized rubber) is developed through the application of statistical mechanical procedures similar to those employed in rubber elasticity theory. Expressions are derived which, within the limitation imposed by the simplifying assumptions, relate the incipient crystallization temperature with the elongation, the degree of crystallinity with the elongation and temperature, and the retractive force at crystallization equilibrium with the elongation at constant temperature. The reciprocal of the absolute temperature for incipient crystallization is predicted to decrease linearly with a simple function of the elongation and the average number of chain segments between cross linkages. Only moderate degrees of crystallinity are predicted at equilibrium. In conformity with requirements of the second law of thermodynamics, equilibrium crystallization decreases the tension in the stretched specimen.

INTRODUCTION

THE tendency for a high polymer to crystallize may be greatly enhanced by deformation. This is particularly true if the polymer

* The work presented in this paper comprises a part of a program of fundamental research on rubber and plastics

Apparent discrepancies between some of these predictions and various observations are attributed to severe departure from equilibrium crystallization when the polymer undergoes crystallization *during* the stretching process. A better approach to equilibrium should be achieved by stretching under conditions which prevent crystallization (e.g., at elevated temperature), then allowing crystallization to proceed at fixed elongation. Few experiments have been performed in this manner, but such results as are available confirm qualitatively the predictions of the theory.

Reasons for the rapid increase in tension which is observed when crystallization occurs during ordinary stretching of rubber are discussed. It is pointed out that crystalline and amorphous regions preferably should not be regarded as separate phases. Likewise, the conversion of amorphous to crystalline polymer does not conform to the definition of a phase transition.

possesses a network structure, in which case the deformation imposes on the structure an orientation which cannot be dissipated by ordinary

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