The Relationship between the BrunauerEmmettTeller Adsorption Isotherm and the New Isotherm of Jura and Harkins

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The Relationship between the Brunauer-Emmett-Teller Adsorption Isotherm and the New Isotherm of Jura and Harkins

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Values for the surface pressure and area of molecules adsorbed on solid surfaces can be calculated from the adsorption equation of Brunauer-Emmett-Teller. Over a wide pressure range these calculated values are in approximate agreement with the two-dimensional equation of state for vapor-condensed films. Since the adsorption equation of Jura and Harkins was derived from this same equation of state, it is concluded that for a great many experimental isotherms, the mathematical agreement between the two adsorption equations is so good that extremely accurate experimental work would be necessary to determine which equation was more nearly correct.

The Brunauer-Emmett-Teller equation gives calculated curves on Gregg-type plots that agree qualitatively with those reported by Gregg for multi-layer adsorptions. Surface-area values obtained from these curves by Gregg's X-point method are generally considerably higher than those that would be obtained by the method of Brunauer-Emmett-Teller.

The limiting area occupied by a molecule (i.e., in a mono-molecular layer) as calculated by the method of Harkins and Jura appears to decrease with decreasing energies of adsorption (i.e., decreasing values of c in the Brunauer-Emmett-Teller isotherm). It is suggested that this decrease is artificial, rather than real, and results from the assumption that the constant a in the two-dimensional equation of state does not vary with changes in the nature of the solid adsorbent.

It is not possible at the present time to suggest that one of the isotherms is to be preferred to the other on theoretical grounds. In general, preference should be given to the one which fits experimental data over the broader pressure range.

SYMBOLS

a = constant of the two-dimensional equation of state (2).

b = another constant of Eq. (2).

b' = intercept on the $k_1\pi$ axis of the straight-line equation (18).

c = constant of the Brunauer-Emmett-Teller adsorption isotherm (1).

k = constant used by Jura and Harkins to convert A values to Σ values.

k_1 = constant of straight-line equation (18).

k_2 = another constant of Eq. (18).

m = slope of straight-line equation (18).

p = pressure.

p_0 = saturation pressure.

v = volume of gas adsorbed per gram of adsorbent.

v_m = volume of gas which would correspond to a mono-molecular layer on one gram of adsorbent.

v_0 = volume of gas adsorbed at saturation per gram of adsorbent.

A = constant of Jura and Harkins adsorption isotherm (9).

B = another constant of Eq. (9).

M = molecular weight of gas.

N = Avogadro's number.

R = gas constant.

T = absolute temperature.

V = volume of one mole of gas.

α = area occupied by each adsorbed molecule in a mono-molecular layer.

π = surface pressure (change in free energy of the solid surface attributable to adsorption).

σ = area per molecule.

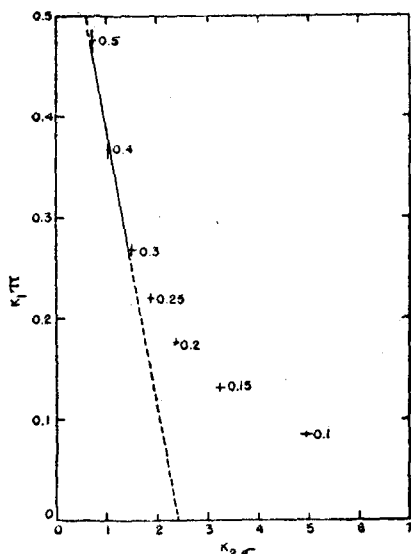Σ = specific surface of adsorbent.

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FIG. 1. Pressure-area plot calculated from Brunauer-Emmett-Teller isotherm with $c=2$; the numbers beside the points are relative pressures.

INTRODUCTION

THE multi-molecular adsorption theory of Brunauer, Emmett, and Teller[1] has been found to be in agreement with a great number of experimentally-determined adsorption isotherms over a fairly extensive range of pressures. In a critical evaluation, Brunauer[2] has concluded that the theory has limited accuracy at very low pressures where adsorbents tend to be strongly heterogeneous, and at high pressures where capillary condensation can occur, but in the pressure range where p/p_0 is 0.05 to 0.35 the agreement of theory and experiment is excellent. The basic equation

$$v = cv_m p p_0/(p_0-p)(p_0-p+cp) \qquad (1)$$

has been found by many investigators to fit the observed data within experimental accuracy over the pressure range given by Brunauer. Extensive use has been made[3] of this equation to calculate the specific surface of solids from v_m.

Jura and Harkins[4] later developed an alternate equation for expressing adsorption isotherms. They considered their equation to have a thermodynamic background, since it was derived by combining the two-dimensional equation of state for condensed mono-layers

$$\pi = b - a\sigma \qquad (2)$$

with the thermodynamic relationship derived by Gibbs for adsorption on solid surfaces [Eq. (678) of the "Equilibrium of Heterogeneous Surfaces"][5] which, for a two-component system at constant temperature, is

$$d\pi = (RT/V\Sigma)(v/p)dp. \qquad (3)$$

Since

$$\sigma = \Sigma V/Nv, \qquad (4)$$

differentiation of Eq. (2) gives

$$d\pi = -(a\Sigma V/N)d(1/v). \qquad (5)$$

By combination of Eqs. (3) and (5), followed by integration, the adsorption isotherm of Jura and Harkins is obtained:

$$\ln p = \ln p_0 + (a\Sigma^2 V^2/2NRT)[(1/v_0^2)-(1/v^2)]. \qquad (6)$$

The constant terms in this equation may be grouped as:
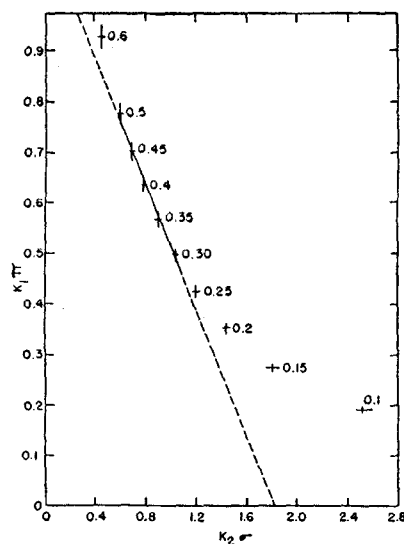
$$A = a\Sigma^2 V^2/2NRT, \qquad (7)$$

FIG. 2. Pressure-area plot calculated from Brunauer-Emmett-Teller isotherm with $c=5$.

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

[2] S. Brunauer, The Adsorption of Gases and Vapors (Princeton University Press, Princeton, 1943), Vol I. Physical Adsorption.

[3] P. H. Emmett, Recent Advances in Colloid Science (Interscience Publishers, Inc., New York, 1942), Vol. I, p. 1.

[4] G. Jura and W. D. Harkins, J. Chem. Phys. 11, 430 (1943).

[5] The Collected Works of J. Willard Gibbs (Longmans, Green and Company, New York, 1928), Vol. I, p. 329.

$$B = \ln p_0 + (A/v_0^2), \qquad (8)$$

so that

$$\ln p = B - A/v^2. \qquad (9)$$

Harkins and Jura[6] found this equation, as well as Eq. (1), to be valid for almost all of the very large number of isotherms that they studied. For nitrogen adsorptions, Eq. (9) generally fits the experimental data over a wider range of pressures than Eq. (1).

Since the specific surface is a factor in the constant A (see Eq. (7)), it can be evaluated from Eq. (9). Harkins and Jura[6] use the relation

$$\Sigma = kA^{\frac{1}{3}} \qquad (10)$$

for this evaluation. They suggest that k has a constant value for any adsorbate at any temperature and recommend a value for nitrogen at $-195.8°$ of 4.06. Specific surface values calculated by this method were almost identical with those calculated by the method of Brunauer-Emmett-Teller. Harkins and Jura[6] state that "this is very remarkable when the great difference between the two theories, one kinetic and the other thermodynamic, is taken into consideration." It is the purpose of this paper to discuss the agreement between these theories and the reason for its existence.
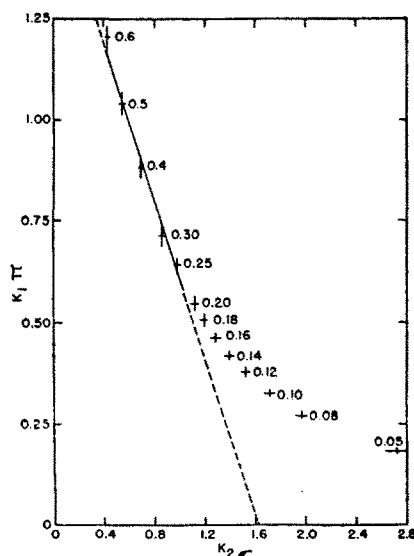

FIG. 3. Pressure-area plot calculated from Brunauer-Emmett-Teller isotherm with $c = 10$.
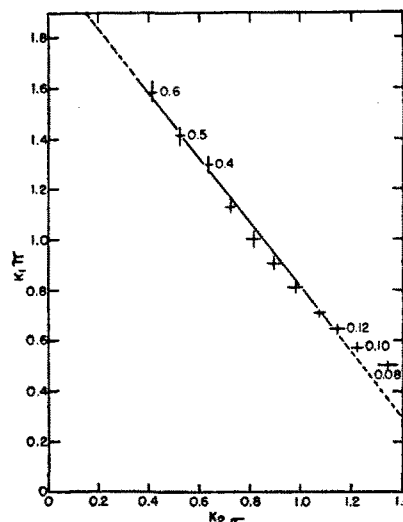

FIG. 4. Pressure-area plot calculated from Brunauer-Emmett-Teller isotherm with $c = 25$.

EQUATIONS RELATING THE THEORIES

(Note: A brief summary of this section was published, under the same title as the present paper, in this journal in November, 1944.)[7]

The mathematical relationship between pressure and adsorption developed by Brunauer, Emmett, and Teller, as expressed by Eq. (1), may be substituted into Eq. (3). The result is:

$$d\pi = (RT/V\Sigma)[cv_m p_0/(p_0 - p) \\ \times (p_0 - p + cp)]dp. \qquad (11)$$

The integration of this equation has been shown[8] to give as the result:

$$\pi = (RTv_m/V\Sigma) \ln(p_0 - p + cp)/(p_0 - p). \qquad (12)$$

Data calculated from Eq. (12) for $c = 50$ were in agreement with Eq. (2) over a wide pressure range.

It is possible to determine the relationship between π and σ, for isotherms obeying the Brunauer-Emmett-Teller equation with widely varying values of c. A substitution of Eq. (1) in Eq. (4) gives:

$$\sigma = \Sigma V(p_0 - p)(p_0 - p + cp)/Nv_m cp p_0. \qquad (13)$$

The terms in Eqs. (12) and (13) that do not vary with p or c may be combined into two

[6] W. D. Harkins and G. Jura, J. Am. Chem. Soc. 66, 1366 (1944).

[7] H. K. Livingston, J. Chem. Phys. 12, 466 (1944).
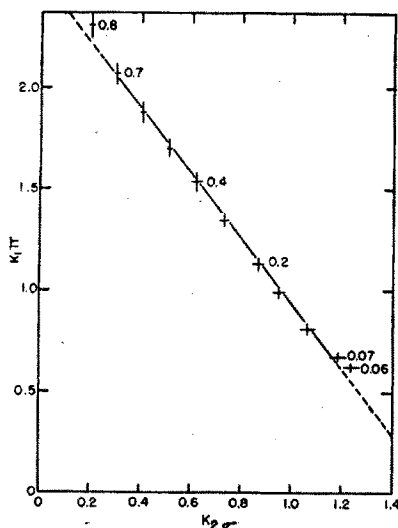[8] H. K. Livingston, J. Am. Chem. Soc. 66, 569 (1944).

FIG. 5. Pressure-area plot calculated from Brunauer-Emmett-Teller isotherm with $c = 50$.

constant terms:

$$k_1 = V\Sigma/(RTv_m \ln 10), \tag{14}$$

$$k_2 = Nv_m/V\Sigma. \tag{15}$$

Then, from Eqs. (12) and (13) the following equations can be formulated:

$$\log(p_0 - p + cp)/(p_0 - p) = k_1\pi, \tag{16}$$

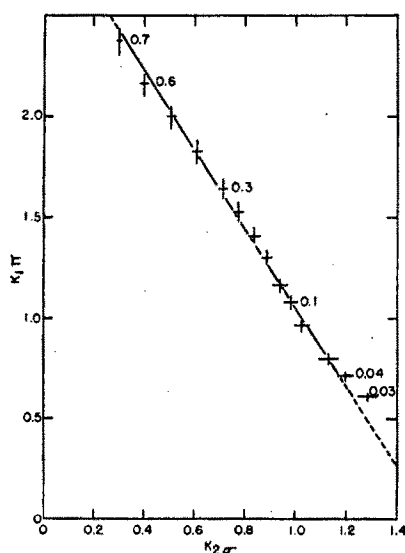$$(p_0 - p)(p_0 - p + cp)/cpp_0 = k_2\sigma. \tag{17}$$

FIG. 6. Pressure-area plot calculated from Brunauer-Emmett-Teller isotherm with $c = 100$.

For any given value of c, the solution of Eqs. (16) and (17) for a series of relative pressures will give $k_1\pi$ and $k_2\sigma$ values that can be examined graphically for the existence of the straight-line relationship:

$$k_1\pi = b' - mk_2\sigma. \tag{18}$$

This, of course, is equivalent to Eq. (2). That is, if values of π and σ calculated from the Brunauer-Emmett-Teller equation are in a straight-line relationship, then the basic assumption made in deriving the equation of Jura and Harkins is satisfied, and the pressure-adsorption isotherm can be expressed by either of the two equations.

CALCULATIONS FOR SELECTED VALUES OF c

Values for $k_1\pi$ and $k_2\sigma$ over a wide range of pressures have been calculated for the following values of c: 2, 5, 10, 25, 50, 100, and 250. The results have been plotted in Figs. 1 to 7. In plotting these data, consideration has been given to the accuracy of experimental adsorption data. In practice, the comparison of data determined experimentally with a theoretical equation is made by applying some test of agreement such as a least-square calculation and, using an assumed value for the accuracy of the experimental data, determining the range of agreement.

Since an assumed experimental accuracy would be used in determining the fit of either the Brunauer-Emmett-Teller of Jura and Harkins isotherms, the region where both appeared to be applicable would increase in extent as the assumed error increased. In plotting Figs. 1 to 7, it has been assumed that π and σ are known with an accuracy of ± 3 percent. The position of the calculated points is indicated, then, by a cross whose dimensions in the horizontal and vertical directions represent 6 percent of $k_2\sigma$ and $k_1\pi$, respectively. On each figure an unbroken straight line is drawn which at each point passes within the ellipse whose axes are the indicated cross. The line actually drawn is the longest possible line fulfilling these conditions. In the region where the conditions no longer apply, a broken line is drawn.

As an example, it will be seen from Fig. 7 that within the assumed limits of ± 3 percent, data that rigorously obey the Brunauer-Emmett-

TABLE I.

c	Constants of straight-line equation (18)		Relative pressures at which the equation fits the data within 3%	
	m	b'	p/p₀, low value	p/p₀, high value
2	0.28	0.68	0.3	0.5
5	.63	1.13	.26	.52
10	.99	1.59	.24	.60
25	1.29	2.09	.11	.62
50	1.61	2.54	.07	.75
100	1.95	3.01	.04	.72
250	2.33	3.66	.07	.50

(These values are based on a recalculation of those given in reference 7 and should be considered to supercede the earlier results.)

TABLE II.

c	Relative pressures at which the equation fits the data within 0.5%	
	p/p₀, low value	p/p₀, high value
25	0.24	0.36
50	.14	.65
100	.14	.55
250	.07	.19
	.38	.65

Teller equation (1) from $p/p_0 = 0.07$ to $p/p_0 = 0.50$, with $c = 250$, would be found, insofar as the accuracy would permit judgment, to obey Eq. (2) (and therefore the Jura and Harkins equation (7)). Similarly, data that rigorously obeyed the Jura and Harkins equation (7) over this pressure range, would be found to obey Eq. (1) (if $c = 250$) over the same range, and no distinction could be made between the two equations.

A summary of the range of pressures over which the two equations agree within 3 percent, for the seven c values studied, is given in Table I. For those c values for which the range is largest, the range of pressures over which the two equations agree within 0.5 percent has also been determined (Table II). Because of the complex form of the line on which the points of Fig. 7 lie, two sets of limits are given for $c = 250$ in Table II. In the Harkins-Jura terminology, this corresponds to the existence of two different condensed phases for the adsorbed vapor.

If accuracy were better than 3 percent, of course, the pressure ranges would be narrowed somewhat. The great majority of experimentally observed c values are from 25 to 250. For these values, the pressure range of agreement is very

wide, covering almost all of the range wherein the Brunauer-Emmett-Teller equation is generally found to be valid. Very accurate experimental work would be necessary to determine which equation was more nearly correct in these cases.

COMPARISON OF THESE RESULTS WITH OTHERS RECENTLY PUBLISHED

Gregg[9,10] has considered adsorption isotherms from the standpoint of two-dimensional equations of state, in the same general manner as Jura and Harkins. Gregg's procedure involves the integration of adsorption data and construction of $\pi\sigma$ vs. $\pi\Sigma$ plots, for a number of systems for which Σ was unknown. He has constructed such plots for adsorbed films on charcoal, mica, sodium chloride, ferric oxide, copper oxide, and silica gel. For gaseous films, such plots give lines extrapolating to $\pi\sigma = RT$ at $\pi = 0$. Gregg assumes, after Schofield and Rideal,[11] that for condensed films the slope of a $\pi\sigma - \pi\Sigma$ curve would be α/Σ.

Gregg has developed two methods for determining surface areas. The first method, applicable to linear plots, depends on the slope being α/Σ, as predicted by Schofield and Rideal. The
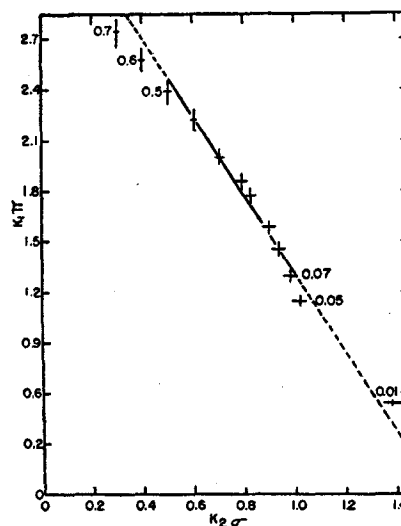

FIG. 7. Pressure-area plot calculated from Brunauer-Emmett-Teller isotherm with $c = 250$.

[9] S. Gregg, J. Chem. Soc. 696 (1942).
[10] S. Gregg, *Proceedings of the Conference on Ultra-fine Structure of Coals and Cokes* (British Coal Utilisation Research Assoc., London, 1944), p. 110.
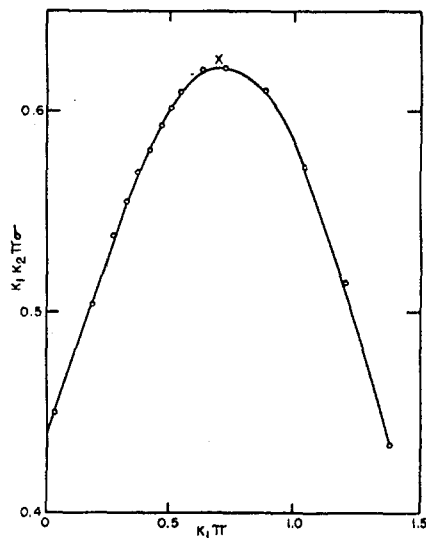[11] R. Schofield and E. Rideal, Proc. Roy. Soc. **A109**, 57 (1935).

FIG. 8. Gregg-type plot calculated from Brunauer-Emmett-Teller isotherm with $c = 10$.
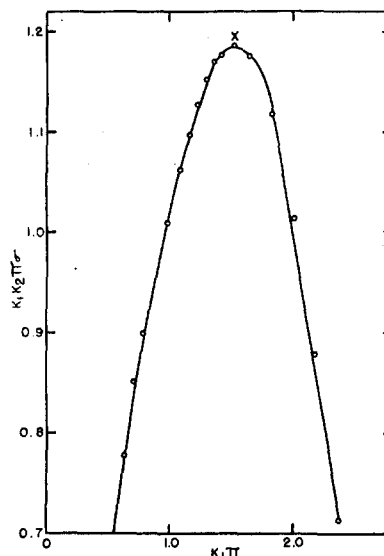

FIG. 9. Gregg-type plot calculated from Brunauer-Emmett-Teller isotherm with $c = 100$.

second method is used in those cases where $\pi\sigma$ vs. $\pi\Sigma$ plots are not linear. Where multi-layer formations occur, parabolic curves are ordinarily observed. Gregg[10] takes the area corresponding to point X (which is essentially the vertex of the curve) to be α, and suggests that this value is approximately the same as would be calculated from the slope below this point. Maggs[12] has found specific surfaces calculated in this way to agree fairly well with those calculated from Eq. (1) (Emmett's method[2]). Gregg[10] suggests that the integration and plotting of Eq. (1) according to his method gives curves that coincide fairly well with the type obtained for his assumed equations of state.

We have used the data plotted in Figs. 3 and 6 to form a $\pi\sigma$ vs. $\pi\Sigma$ plot of the Gregg type. The curves (Figs. 8 and 9) closely resemble several of those that Maggs[12] has calculated from experimental data. Gregg's first method, which assumes that $\sigma = \alpha$, requires that for a plot of $k_1 k_2 \pi\sigma$ vs. $k_1\pi$, the slope be $k_2\sigma(=k_2\alpha=1)$ (see Eq. 19). Since the curves drawn in Figs. 8 and 9 are not straight lines, it is not proper to apply this method, but it can be stated that in neither case is a slope of unity approached by an appreciable linear portion of the section of the

[12] F. Maggs, *Proceedings of the Conference on Ultra-fine Structure of Coals and Cokes* (British Coal Utilisation Research Assoc., London, 1944), p. 95.

curves that is shown. If the second (X-point) method is used, the areas corresponding to the vertex of the curves (indicated by X in Figs. 8 and 9), as obtained from the original $k_1\pi - k_2\sigma$ data, should be $\sigma = \alpha$. Actually, the areas are $\sigma = \alpha/1.16$ for $c = 10$ and $\sigma = \alpha/1.29$ for $c = 100$. This shows that an estimation of the section area (α) by this method would be appreciably in error for adsorptions that follow the Brunauer-Emmett-Teller equation.

Emmett[13] has recently compared the Brunauer-Emmett-Teller and Jura and Harkins equations directly by solving Eq. (1) for v at various pressures and plotting the results according to Eq. (9) [i.e., $\log p/p_0$ vs. $(1/v^2)$]. The calculations were made for the following c values: 2, 5, 10, 25, 50, 100, 250, and 1000. This is equivalent to the operation carried out in the present paper, but Emmett's calculations were made with $p - v$ data rather than $\pi - \sigma$ data. That is, in the present paper, Eq. (1) was integrated (by means of the Gibbs equation) and substituted into Eq. (2), from which the Jura and Harkins equation (9) was derived, while Emmett used Eqs. (1) and (9) in their original forms.

It is interesting to compare the two results, especially since the same c values were used, except for $c = 1000$. In both cases curved lines

[13] P. H. Emmett, J. Am. Chem. Soc. **68**, 1784 (1946).

were obtained. Emmett has concluded that, inasmuch as curved lines are obtained, the statement in reference 7 that straight lines are obtained within 3 percent is misleading. This is no doubt true, if the significance of the 3 percent limitation (which unfortunately was not stressed in reference 7) is not appreciated. It should be emphasized that the 3 percent error allowed applies to $\pi - \sigma$ data, not $p - v$ data.

Emmett has stated that his data, as plotted in Figs. 1 and 2 of his article, approximately coincide with a straight line over an appreciable pressure range. Within the pressure range $p/p_0 = 0.11$ to 0.40, and for the common c values of 25 to 250, his data show a fairly reasonable agreement to exist between the two isotherms. This leads to the same conclusion arrived at from a consideration of Figs. 1 to 7, namely, that very careful experimental work would be necessary in many cases to determine which isotherm is the more accurate. In comparing Emmett's plots with those given in this paper, consideration must be given to the fact that his method of plotting is much more sensitive to variations in v, since he uses v^{-2} as an abscissa, rather than σ which is a function of v^{-1}.

SPECIFIC SURFACES CALCULATED FROM THE TWO ISOTHERMS

Emmett[13] has made the interesting observation that cross-sectional areas (section areas) of adsorbed molecules calculated from the Jura and Harkins equation vary with c, if they are calculated from the synthetic data obtained by substituting Eq. (1) in Eq. (7). His plot shows the calculated section area of nitrogen to vary from 13 to 20 A^2/molecule as c varies from 30 to 300. This same type of calculation can be made from the data of Table I.

The section area, α, is defined by the equation

$$\alpha = V\Sigma/Nv_m = 1/k_2. \qquad (19)$$

It bears a definite relationship to the constants of Eq. (18). This equation may be put in the form

$$\pi = b'/k_1 - (mk_2/k_1). \qquad (20)$$

Comparison with Eq. (2) shows that the term (mk_2/k_1) must be equivalent to a. Therefore

$$m = a\alpha k_1 = \frac{a\alpha V\Sigma}{RTv_m \ln 10} = \frac{Na\alpha^2}{RT \ln 10}. \qquad (21)$$

If, as was assumed by Harkins and Jura,[6] a is a constant for a given adsorbent at constant temperature, the m values in Table I may be used to calculate α as a function of c. It will be assumed that $\alpha = 16 \, A^2$ at $c = 100$ (which is the value read from Emmett's Fig. 3). The results of this calculation are plotted in Fig. 10. While this plot covers a different range of c values than Emmett's Fig. 3, the two seem to be in close agreement.

Emmett reports a trend in experimental α values roughly coinciding with the derived curve. While this may be a generally valid result, it should be pointed out that a may not necessarily be a constant for different c values. Harkins and Jura made this assumption because it is known that insoluble mono-layers on water tend to show no change in a when the pH or electrolyte content of the water sub-phase is changed. Such changes might have much less effect on surface forces than would result from changes in the solid adsorbent that cause large changes in c. Certainly a comparison between adsorptions of the same vapor on two adsorbents differing in c values by a factor of 10 or more might be expected to show appreciably different a values. It would seem likely then, that the values of k given by Harkins and Jura[6] for different ad-
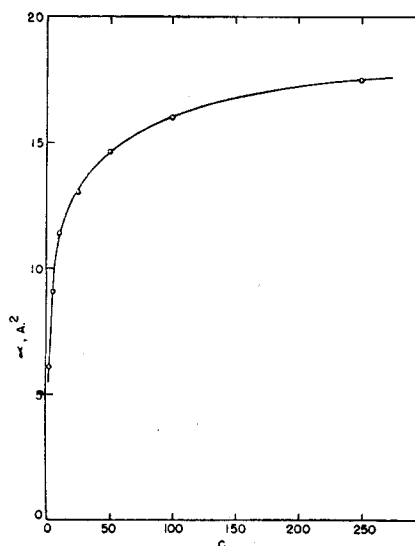

FIG. 10. The cross-sectional area (α) of molecules calculated by the Harkins and Jura method from the slope of Figs. 1–7 (assuming $\alpha = 16$ at $c = 100$).

sorbents might not always have the unique values assigned.

POSSIBILITY OF A CHOICE BETWEEN THE TWO ISOTHERMS

It is conceivable that a mathematical analysis of the two isotherms would suggest a basis for preferring one to the other. No such choice can be made as a result of the present analysis. The fact that the two equations are both equally in agreement with many of the experimental isotherms determined during the past ten years promises to make such a choice particularly difficult. If it is a fundamental property of adsorbed films under these experimental conditions to obey the two-dimensional equation of state of condensed films, then it might be considered fortuitous that the equation derived by Brunauer, Emmett, and Teller, with appropriate constants, expresses the adsorption isotherm over a considerable pressure range. On the other hand,

if the kinetic theory of these authors, from which their equation was derived, is an exact expression of the performance of vapors and adsorbents at moderate relative pressures, for a great many systems the surface pressure and area will correspond to the two-dimensional equation of state expressed by Eq. (2), and therefore will be in agreement with the Jura and Harkins isotherm.

The nature of the relationship between the two isotherms has been most recently summarized by Jura and Harkins,[14] who concluded that "it is apparent that there is no conflict." It was predicted that new developments in theoretical and experimental studies of phase transitions would improve the agreement. In investigations of this sort, consideration should be given to the mathematical relationship between the equations that has been demonstrated by Emmett[13] and in the present paper.

[14] G. Jura and W. D. Harkins, J. Am. Chem. Soc. 68, 1941 (1946).

The Adsorption of Hydrogen on Tungsten Powders

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An analysis of the extensive experimental data of Frankenburg on the adsorption of hydrogen by metallic tungsten powder between −194 and 750°C has been made, using the Fowler-Guggenheim treatment of adsorption phenomena as the mode of approach. It has not been found possible to interpret the data in terms of interaction between the adsorbed species on a *uniform* adsorbent surface. It is shown that the experimental data can be interpreted on the basis of a non-uniform surface without interaction, the heterogeneity of the surface being specified in terms of an exponential distribution of sites given by the distribution function $N = ce^{-\chi/\chi_m}$, where χ represents the energy difference between the lowest energy state of the gas and the lowest energy of the adsorption complex. Such a distribution function yields the experimentally observed relation $d \ln p/d \ln \theta = $ constant at constant temperature. Such a heterogeneity is especially significant in the case of tungsten metal which hitherto has been treated as an essentially uniform surface. The quantity χ_m has been found to vary with the temperature. The significance of this variation has been briefly explored.

A COMPREHENSIVE study of the adsorption of hydrogen on tungsten powders has been recorded by W. G. Frankenburg,[1] and he has presented a series of isotherms between −194° and 750°. Special attention was given to

[1] J. Am. Chem. Soc. 66, 1827 (1944); 66, 1838 (1944).

the cleanliness of the metal surface, and the hydrogen was adsorbed rapidly at the temperatures employed. These data form an excellent example of an adsorption equilibrium in a localized mono-layer. Frankenburg's analysis of his data led to an empirical relation, the logarithm