to the distribution of polymer compositions. For a ternary system, the method is as follows:

The computation makes use, alternatingly, of equations (2) and (5), evaluating the total in consecutive steps. The polymer compositions corresponding to the initial monomer compositions are calculated from equation (2). This gives a value of $(A_p - A)_0$ (Fig. 4) which is assumed to be constant for limited variations in A. Equation (5) gives the per cent. conversion for such a variation dA. From A_1 ($= A + dA$), and the corresponding B_1 and C_1, the new polymer compositions are calculated from equation (2), thus giving $(A_p - A)_1$, which is used for the next conversion calculation according to equation (5).

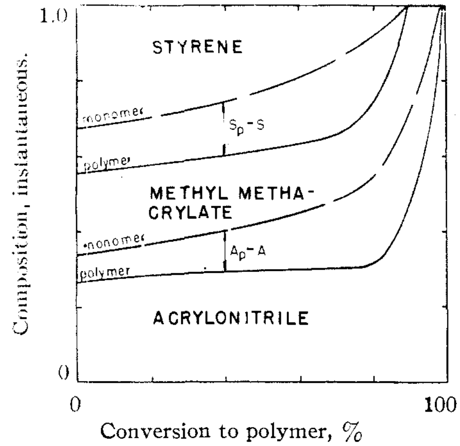

Fig. 4.—Compositions of monomer and polymer *vs.* conversion, for an equimolar mixture of acrylonitrile, methyl methyacrylate and styrene.

If $(A_p - A)$ is found to vary over the interval dA, a more suitable value for $(A_p - A)$ can be chosen (for example, the average of $(A_p - A)_0$ and $(A_p - A)_1$), and the conversion recalculated. To reduce the number of calculations this preferable value for $(A_p - A)$ is anticipated from the trend of the curves. In regions where $(A_p - A)$ is changing rapidly, precision is maintained by calculation over smaller intervals.

Figure 4 shows the conversion–composition relationship obtained by this method for an equimolar mixture of acrylonitrile, methyl methacrylate and styrene.[11,5]

The first polymer is richer in styrene and poorer in acrylonitrile than the monomer; consequently the monomer is depleted of styrene and enriched in acrylonitrile. As polymerization proceeds, compositions of both unreacted monomer and instantaneous polymer change; but the change in the latter is less. Thus, up to 70% conversion, the polymer aggregate is fairly uniform in composition. At that point, however, the changes become more marked. At 90% conversion, the styrene is virtually gone; and the last 1% of polymer is almost pure acrylonitrile.

In a technical process, if uniformity of polymer composition were desired, the polymerization could be stopped at approximately 70% conversion.

For systems of more than three components, computation of instantaneous monomer–polymer relationships becomes more tedious, but with this accomplished, the calculation of the conversion from equation (5) is just as easy as for a ternary or binary system.

Acknowledgment.—The author wishes to thank Dr. Ernest P. Irany for helpful discussion and criticisms.

Summary

A new method of computation of the composition distribution of copolymers is proposed which permits evaluation of systems containing any number of components.

NEWARK, N. J. RECEIVED[12] APRIL 17, 1946

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[11] Lewis, Mayo and Hulse, THIS JOURNAL, **67**, 1701 (1945).

[12] Presented before the High Polymer Forum at the Atlantic City meeting of the American Chemical Society, April, 1946.

[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Multilayer Adsorption Equations

BY P. H. EMMETT

Brunauer, Emmett and Teller[1] have suggested that, if low temperature adsorption data are plotted according to the equation

$$\frac{p}{v(p_0 - p)} = \frac{1}{V_mC} + \frac{(C - 1)}{V_mC}\frac{p}{p_0} \qquad (1)$$

a straight line is obtained over a relative pressure range extending from about 0.05 to 0.35. V_m, in this equation, represents the volume of adsorbate required to form a monolayer over the solid adsorbent. v is the volume of gas adsorbed at relative pressure p/p_0; and C is a constant. A simple multiplication of the number of adsorbed molecules corresponding to V_m, by their average cross-sectional area, would then yield an absolute value for the surface area of the solid being measured. This equation has been applied successfully to a large number of finely divided and porous solids.

Recently, Harkins and Jura[2,3] have published a

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[1] Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 310 (1938).

[2] Harkins and Jura, *ibid.*, **66**, 919 (1944).

[3] Harkins and Jura, *ibid.*, **66**, 1366 (1944).

series of papers presenting an entirely new[3a] method for measuring the surface areas of finely divided or non-porous solids without having to resort to any assumption as to the cross-sectional area of the adsorbate molecule. Their method consists of measuring the heat of immersion of a finely divided solid (titanium oxide) in water after the solid has picked up sufficient water vapor (several statistical layers) to cause the heat of immersion per gram of dry solid to be substantially independent of the amount of water adsorbed. By assuming that the heat of immersion of such a sample per sq. cm. is the same as that of water droplets, they divide the total evolved heat by 118.5 to obtain a value of the surface area directly. A comparison of the result obtained by this method on finely divided titanium dioxide with the result obtained by using equation 1 has shown almost perfect agreement. An area of 13.8 sq. meters per gram was obtained by the one method and of 13.9 sq. meters per gram by the other; the latter value involved the assumption that the cross-sectional area of the nitrogen adsorbate molecule was 16.2 sq. Å.

More recently, Harkins and Jura[4] have also found an alternative method of plotting the low temperature gas adsorption data to obtain a value for the surface area of finely divided porous or non-porous solids. They have shown that plotting the data according to the equation

$$\log p/p_0 = B - A/v^2 \qquad (2)$$

where A and B are constants, and the other symbols are the same as for equation 1, enables them to calculate the surface area of a sample of adsorbent from the equation

$$\text{Surface area} = k(A)^{1/2} \qquad (3)$$

where A is the slope of the $\log p/p_0$ *vs.* $1/v^2$ plot. The value of k for nitrogen was evaluated by the use of the surface area obtained from experiments on the heat of immersion of titanium dioxide and was found to be equal to 4.06 if v is expressed in cc. of gas at standard temperature and pressure.

By using equation 3 and by assuming a constant k value at $-195°$, they measured the surface area of a great variety of porous or non-porous solids. They also pointed out that, to obtain surface area values by the B.E.T. plot of the nitrogen adsorption data that agreed with those found by the use of equations 2 and 3, it was necessary to assign to the adsorbed nitrogen molecules cross-sectional area values ranging from about 13.6 to 16.9 sq. Å. though occasionally a value as high as 20 or 21 sq. Å. would have to be used.[5]

There have been several attempts to explain the reason for equations 1 and 2 both yielding straight-line plots for the same adsorption data over a considerable range of pressure. The purpose of the present paper is to show how the limits within which equations 1 and 2 mutually agree depend upon the heat of adsorption and then to discuss various aspects of the significance, usefulness and limitation of the two equations for surface area measurements.

Influence of the Value of C on the Harkins and Jura Plots.—The constant C of equation 1 is related to the heat of adsorption and the heat of liquefaction by the equation

$$C = \frac{b_2 a_1}{b_1 a_2} e^{(E_1 - E_L)/RT}$$

where E_1 is the average heat of adsorption of molecules in the first layer, E_L is the heat of liquefaction and a_1, b_2, a_2 and b_1 are constants. Equation 1, upon being transformed may be written as

$$v = \frac{CV_m p/p_0}{(1 - p/p_0)(1 + (C - 1)\, p/p_0)} \qquad (4)$$

In Figs. 1 and 2 are plotted, according to the Harkins and Jura method, values of $1/v^2$ against p/p_0, the values of v having been calculated from equation 4 for different values of C and of p/p_0.

It is evident at once that the region usually resulting in a straight line B.E.T. plot (the region between 0.05 and 0.25 to 0.35 relative pressure) gives an approximately straight line Harkins and Jura plot only for C values of 50 to 250. For C values of 10, 5 or 2 (Fig. 2) no straight line section of the Harkins and Jura plot exists at relative pressures lower than 0.4. For C values as high as 1,000, the straight line portion of the plot, common to both the Harkins and Jura and B.E.T. plotting, is limited to the region 0.01 to about 0.13 In other words, the Harkins and Jura type of plot will not give a straight line for experimental data over any appreciable portion of the 0.05 to 0.35 range for C values of about 25 or less, *if* the data plot up as straight lines over this relative pressure range by B.E.T. plots; also for C values higher than about 250, two straight lines of quite different slopes are required to cover the relative pressure range 0.05 to 0.35 by a Harkins and Jura plot of the B.E.T. isotherm.

A second interesting correlation can be obtained with the help of Figs. 1 and 2. If one calculates the cross-sectional area that would have to be assigned to the nitrogen molecule in order to obtain from a B.E.T. plot a surface area in agreement with that obtained by use of equation 2 and 3, one finds that for $C = 50$, the value is 13.6 sq. Å. per molecule; for $C = 100$, the value is about 15.8; for 250, 18.6; and for 1,000, 24.6 sq. Å. It is easy to understand, therefore, why Harkins and Jura have found a variation in the apparent

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(3a) Harkins and Jura were the first to suggest the general application of this method for surface area measurements on finely divided, non-porous solids. It is interesting to note that Patrick and Grimm, *ibid.*, **43**, 2144 (1921), accounted for the heat of immersion of their silica gel samples in water by assuming that the "envelope of water" considered to be present over the surface of their gel completely disappeared on immersion with the resulting evolution of 118.5 ergs per sq. cm. On this basis, they calculated the surface area of their gel to be 650 sq. m. per g. and remarked that this figure seemed in good agreement with other surface area estimates then available.

(4) Harkins and Jura, THIS JOURNAL, **66**, 1366 (1944).

(5) Harkins and Jura, *J. Chem. Phys.*, **11**, 431 (1943).

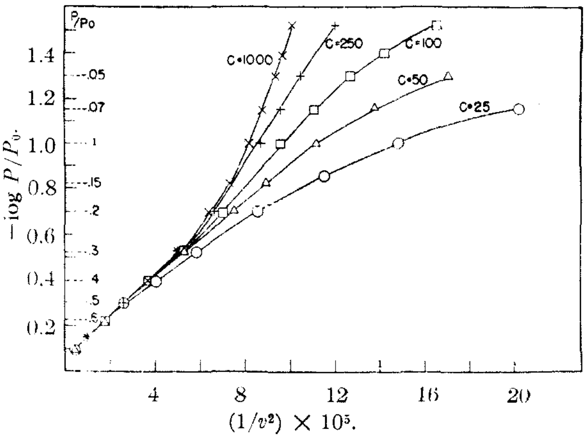

Fig. 1.—Influence of the constant C (equation 1) on the agreement between B.E.T. equation 4 and Harkins and Jura's equation 2. Volume of gas adsorbed, v, is calculated by equation 4 for V_m = 100 and C = 25, 50, 100, 250 and 1,000 respectively.

	C	Å.²/mol.	P/P_0 range
○○	25	11.7	.13 to .35
△△	50	13.6	.08 to .35
□□	100	15.8	.05 to .35
++	250	18.6	.03 to .3
××	1000	24.6	.03 to .13

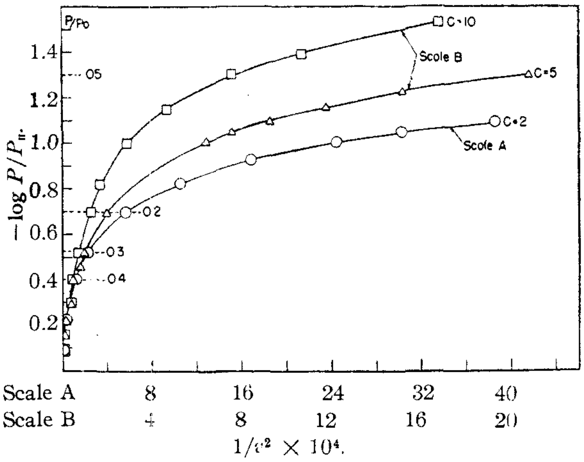

Fig. 2.—Influence of the constant C (equation 1) on the agreement between B.E.T. equation 4 and Harkins and Jura's equation 2. Volume of gas adsorbed, v, is calculated by equation 4 for V_m = 100 and for C = 2, 5 and 10.

	C	Å.²/mole	P/P_0 range
○○	2	3.7	0.2 to 0.4
△△	5	6.8	0.2 to 0.4
□□	10	9.1	0.2 to 0.4

cross-section extending from 13.7 to 21 sq. Å. for nitrogen in view of the fact that examples of nitrogen isotherms are known having C values over the entire range 50 to 1,000.

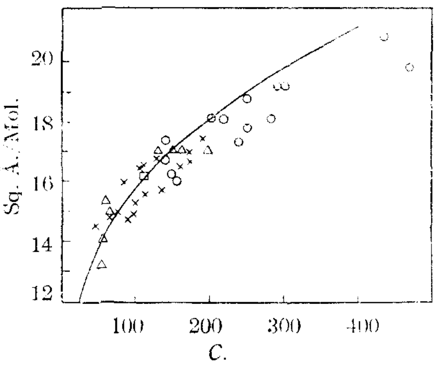

Fig. 3.—Relation between the cross-sectional area value that has to be assigned to bring agreement between surface areas calculated by Harkins and Jura's equation 2 and B.E.T. equation 4 as a function of the constant C in equation 4: △, misc. solids; ○, carbon black; ×, metals; □, TiO_2 Harkins and Jura; ——, calculated from Harkins and Jura plot of B.E.T. equation 4.

Even though Fig. 1 clearly indicates that one must expect a variation with C of the apparent cross-sectional area of the nitrogen molecule required to give agreement between the Harkins and Jura and the B.E.T. plots, it seemed desirable to ascertain whether actual data show such a correlation. In Fig. 3 are presented experimental values of C obtained mostly in the author's laboratories for nitrogen on a variety of solids as a function of the calculated cross-sectional area that has to be assigned to give agreement between the areas resulting from plots by equation 1 and those obtained by equations 2 and 3. No points are plotted for data failing to give straight line plots of equation 2 over at least part of the range 0.05 to 0.35. If two straight line portions occurred in the plots in this relative pressure range, the required molecular cross-section in each case was obtained by weighing the values in proportion to the fraction of the 0.05 to 0.35 relative pressure range covered by each straight line. On the same plot are shown, as a solid curve, the molecular areas shown in Fig. 1 to be required for different C values, to give agreement between the linear Harkins and Jura and the B.E.T. plots of equation 1. It is very evident that the data confirm the conclusions drawn from Fig. 1. On the basis of these data and calculations, the author is of the opinion that good agreement between the B.E.T. (using 16.2 sq. Å. as the cross-sectional area of the nitrogen molecule)[5a] and the Harkins and Jura plots will be obtained only for C values between 100 and 150. For C values of 25, the Harkins and Jura area value would be 40% lower, and for C = 1,000, 35% higher than that obtained by the usual B.E.T.

(5a) It has always been admitted that the choice of the cross-sectional area of the adsorbed nitrogen molecule is subject to considerable uncertainty. On the basis of hexagonal close packing, the values are 13.8 and 16.2 sq. Å. as calculated from the density of solid and liquid nitrogen, respectively. Measurements by Harkins and Jura on six non-porous oxides point to the value 16.2 sq. Å. as being correct. In spite of this nice agreement, the writer believes that one should, for the present, use the value 16.2 sq. Å. but keep in mind the possibility that this value may not be the most nearly correct one and that possibly the correct molecular area value for one solid may not be correct for another because of difference in lattice spacing.

plot using 16.2 sq. Å. per nitrogen molecule. For C values less than about 25 and greater than about 250, the Harkins and Jura plots will not yield a straight line over the entire range 0.05 to 0.3, *provided* the adsorption data yield a straight line in this region when plotted according to the B.E.T. equation.

Discussion

The most striking conclusion that one should reach on examining closely the theories upon which equations 1, 2 and 3 are based is that there is in reality comparatively good agreement between the method for measuring surface areas of finely divided and porous solids by equations 2 and 3 as suggested by Harkins and Jura[4] and the method using equation 1 as developed by Brunauer, Emmett and Teller.[1] When one remembers that only a few years ago there were no methods available for getting such surface areas more accurately than to an order of magnitude, he will realize that the two approaches are in reality beautiful confirmations of each other. Furthermore, there is no conflict between the two approaches as to the theory of adsorption. The B.E.T. approach attempts to explain the form of the adsorption curve by postulating the existence of multilayers of adsorbed molecules and by setting up certain kinetic equations based upon the rates of adsorption and desorption of the molecules in the various layers. The Harkins and Jura equations do not formulate a theory of adsorption but are in reality rather expressions of the fact that the same empirical equation relating surface pressure π to the average area per adsorbed molecule, σ

$$\pi = b - a\sigma \qquad (5)$$

that has been shown to apply to insoluble films on water also appears to apply as a rule to the physical adsorption of gas on solids.

It is only when one attempts to assess the value of equation 1 in comparison to equations 2 and 3 for fixing the values for the surface area of finely divided solids within limits closer than about ±35% that one is forced to examine more closely the premises on which each method rests and to attempt to assign reasons for the agreements and the disagreements that are encountered. It must be admitted that, at the present time, it is simply impossible within such narrow limits to state with certainty which of the two methods gives on an average the more nearly correct surface area values. Nevertheless, for the sake of clarity, it seems worth while to point out certain facts relative to the characteristics and limitations of the two methods:

1. No one can apparently any longer doubt the existence of what might be called phase changes in gas–solid adsorption systems. The peculiar adsorption results obtained by Wooten and Brown[6] for ethylene on alkaline earth oxides at −183°, the very striking adsorption results recently reported for heptane on iron oxide[7] and possibly the measurements of Shereshefsky and Weir[8] for nitrogen on glass spheres, all appear to be explainable on such a basis. However, according to Harkins and Jura[4] the only phase to which equation 5 applies is one of the "condensed phases." The spectacular phase change of the type illustrated by heptane on iron oxide in which the volume of adsorption rises abruptly at a given relative pressure is, according to Harkins and Jura, a "first order" phase change and represents a transition from a "gaseous" to a "liquid expanded" surface phase. The existence of condensed phases is much less evident from the adsorption isotherm plots and really becomes apparent only when equation 5 is actually applied and found to fit the experimental data.

Two points should be made perfectly clear in regard to these phase transitions. In the first place the applicability of equation 5 to experimental data is no reason for concluding that equations 2 and 3 will yield more reliable surface area values than equation 1. It must be kept in mind that equation 5 is empirical and that the k used in equation 2 is in reality equal to $10^{16}V^2\Sigma^2a/2RTN_0$, where V is the gaseous molal volume, Σ is the area, N_0 is Avogadro's number and a is an empirical constant. There seems to be no more reason for expecting "a" to be independent of the adsorbent than for expecting the area occupied by each adsorbate molecule in a monolayer to be independent.

The second fact to be noted in connection with these phase changes is that they do not interfere with the measurement of the surface areas by adsorbed nitrogen isotherms and equation 1. No phase change has been described so far for adsorbed nitrogen over the range 0.05 to about 0.3 usually employed for B.E.T. plots. For other gases, and for certain solids, phase changes may cause complications in surface area measurements. For example, the phase change of the type found by Wooten and Brown[6] for ethylene occurred at relative pressure between 0.2 and 0.4. This would certainly interfere with the application of equation 1. However, it also probably interferes[8a] with the application of equations 2 and 3.

Presumably it will be necessary to choose adsorption gases in such a way as to avoid complications due to phase changes. From this point of view, nitrogen at −195° seems to be one of the preferred adsorbates.

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(6) Wooten and Brown, THIS JOURNAL, **65**, 113 (1943).

(7) Jura, Loeser, Basford and Harkins, *J. Chem. Phys.*, **14**, 117 (1946).

(8) Shereshefsky and Weir, THIS JOURNAL, **58**, 2026 (1936).

(8a) The exact pressure range over which "condensed" phases occur cannot be predicted for a given adsorbate without some experimental data. Hence, possibly the Harkins and Jura plot (equation 2) of ethylene data might be linear in the region above 0.4 relative pressure. Indeed, it is not intended to imply by Figs. 1 to 3 that straight-line plots of log p/p_0 against $1/v^2$ are never obtained for actual data for small values of C. It is quite possible that the linear Harkins and Jura plots for some adsorbates might cover a considerable range of relative pressures in the range 0.4 to 1.0.

2. Equation 2 may be defined[9] as "thermodynamic" in the sense that it is derived from the application of Gibbs adsorption equation to equation 5. On the other hand, equation 1 was originally derived on a purely kinetic basis. To those to whom a thermodynamic approach may be preferable, the B.E.T. equation has recently been made more respectable by being derived independently by Cassie[10] and by Hill[11] by a thermodynamic, or, more correctly, a statistical thermodynamic, approach. Hill has criticized Cassie's derivation but has shown that an alternative derivation also leads to equation 1.

The constant C in equation 1 is shown by Cassie[10] to be actually $j_s/j_L e^{+w/RT}$ where j_L and j_s are the partition functions for the molecules adsorbed in second or higher layers and in the first layer, respectively, and w is the amount by which the heat of adsorption in the first layer exceeds the heat of condensation in the second and higher layers. Cassie estimates that the theoretical value for the ratio of the partition functions should be about 1/50 and points out that a value of 1/50 for this ratio compared to an assumed value of unity for the coefficient a_1b_2/a_2b_1 in the definition of C, given by Brunauer, Emmett and Teller,[1] will cause the apparent heat of adsorption of N_2 at -195° calculated from the B.E.T. equation to be low by (2.303 RT log 50) calories. This calculation explains, in part at least, a possible reason for the low heat of adsorption values usually obtained from the C of B.E.T. plots.[12] As a matter of fact, the quantity (2.3 RT log 50) accounts almost exactly for the difference between the $E_1 - E_L$ value for benzene adsorption on titanium dioxide (2,600 calories) and the "heat of demersion" (5,200 calories) measured by Harkins and Boyd.[12] It also agrees with the amount (600 to 900 calories) by which, according to experimental measurements by Beebe[13] and co-workers, the average heat of adsorption of nitrogen in the first layer on two different carbon blacks exceeds the value that one would calculate from the constant C of the B.E.T. equations for nitrogen isotherms on these same two carbon blacks. It is, of course, too early to conclude that Cassie's calculation of the coefficient a_1b_2/a_2b_1 as $\sim 1/50$ is generally applicable. As a matter of fact, the ratio of the partition functions will certainly depend on both the adsorbate and adsorbent. It, nevertheless, seems of interest that for these examples, at least, his estimate is certainly of the right order.

3. Livingston[9] has stated that the Harkins and Jura plot of the B.E.T. equation would, within 3%, give a straight line over relative pressures extending from 0.2 to 0.4 at $C = 2$; 0.25 to 0.5 at $C = 5$; 0.15 to 0.5 at $C = 10$; 0.14 to 0.6 at $C = 25$; 0.07 to 0.7 at $C = 50$; 0.04 to 0.6 at $C = 100$ and 0.07 to 0.5 at a C value of 250. An inspection of Figs. 1 and 2 makes it evident that such a statement is very misleading. Only for $C = 50$ is an approximately linear plot obtained over the limits mentioned by Livingston. For the other mentioned values of C, either smooth curves or two straight lines exist in the relative pressure range cited. Furthermore, if one approximates the curves for $C = 2$, 5 and 10 by straight lines over the relative pressure range designated by Livingston, one finds that the cross-sectional area, that would have to be assigned to the nitrogen molecule for B.E.T. plots to give agreement with the Harkins and Jura value, would be about 4, 7 and 9, respectively, for $C = 2$, 5 and 10. Hence, the use of Harkins and Jura plots for such C values would lead to a discrepancy factor of 2 to 4 with values calculated from B.E.T. isotherms with 16.2 sq. Å. assumed for the cross-section of the nitrogen molecules.

4. It is frequently pointed out that the Harkins and Jura equation 2 fits experimental data over a much larger range of relative pressures than does the B.E.T. equation. Admittedly, the B.E.T. equation does not hold above relative pressures of about 0.35. However, Anderson[14] has recently shown that if $p/p_0/v(1 - Kp/p_0)$ is plotted against p/p_0 where K has a value that for nitrogen adsorptions is usually about 0.7, a straight line plot is obtained over the entire range from 0.05 to 0.7 relative pressures. He points out that the existence of a constant such as K having a value of 0.7, is equivalent to assuming that the heat of adsorption in the second and higher layers is less than the heat of normal liquefaction by about 50 calories, or to introducing a small entropy term that would result from the multilayers being more ordered than a liquid phase. Accordingly, the deviation of the usual B.E.T. plot from linearity at pressures as low as 0.3 to 0.35 may perhaps be blamed not so much upon any lack of soundness of the B.E.T. approach, but upon the lack of refinements required for the relative pressure range 0.35 to 0.7.

5. In fairness to the work of Harkins and Jura, it must be pointed out, in conclusion, that truly phenomenal agreement has been obtained by them for surface areas of six supposedly non-porous solids using equations 2 and 3 with k value of 4.06 for nitrogen at -195°; 3.83 for water at 25°; 13.6 for n-butane at 0°; and 16.9 for n-heptane, at 25°. Table III of their paper is reproduced here as Table I to illustrate the closeness of the agreement. In all cases, the k values were obtained for the isotherms on titanium oxide for which a surface area of 13.8 sq. meters per gram was available from heat of immersion experiments. In the same Table it will be noticed that the areas from the B.E.T. plots of different adsorbates give less satisfactory agreement than the

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(9) Livingston, *J. Chem. Phys.*, **12**, 462 (1944).

(10) Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).

(11) Hill, *J. Chem. Phys.*, **14**, 263 (1946).

(12) Harkins and Boyd, This Journal, **64**, 1195 (1942).

(13) Beebe, Biscoe, Smith and Wendell, to be published: Paper 38, Division of Rubber Chemistry presented at the Spring Meeting of the American Chemical Society, Atlantic City, N. J., April 12, 1946.

(14) Anderson, This Journal, **68**, 686 (1946).

TABLE I

AREAS OF SOLIDS CALCULATED BY THE NEW METHOD OF HARKINS AND JURA AND BY THAT OF BRUNAUER, EMMETT AND TELLER[a]

Areas in square meters per gram

	New method of Harkins and Jura				B.E.T. method				
	N_2	H_2O	*n*-Butane	*n*-Heptane	N_2 σ = 16.1	H_2O 14.8	H_2O 11.3	*n*-Butane 56.6	*n*-Heptane 64.0
TiO_2 (Standard)	13.8	13.8	13.8	13.8	13.8	13.8	10.5	13.8	13.8
TiO_2 II	8.7	8.4		8.7	8.6	11.7	8.8		8.7
SiO_2 (Quartz)	3.2	3.3		3.3	3.2	4.2	3.2		3.6
$BaSO_4$	2.4	2.3	2.2	2.3	2.4	2.8	2.1	2.7	2.4
$ZrSiO_4$	2.9	2.7			2.8	3.5	2.7		
$TiO_2 + Al_2O_3$	9.6	11.8			9.5	12.5	9.5		

[a] This is Table III of the paper by Harkins and Jura (ref. 3) with a column of calculations for the areas by B.E.T. method using water isotherms with an assumed cross-section of 11.3Å.^{2} for the water molecule.

Harkins and Jura plots where cross-sectional areas (in sq. Å. per molecule) of 14.8 for water; 56.6 for *n*-butane; and 64 for *n*-heptane are arbitrarily assigned. However, an assignment of 11.3 sq. Å. to water in place of 14.8 gives, as shown in Table I, substantially as good average agreement as obtained by Harkins and Jura, there being only one serious discrepancy in each comparison. Nevertheless, one gets such good agreement only by assigning values of 11.3, 56.6 and 64, for water, *n*-butane and *n*-heptane, rather than 10.5, 32 and 45 sq. Å. that one would calculate from the density of the liquids in the prescribed manner. It, therefore, seems that the cross-sectional areas that have to be assigned to adsorbate molecules to obtain areas agreeing with those calculated from nitrogen isotherms are sometimes larger than those calculated from liquid densities by factors of as much as 1.5. This is consistent with the results reported by Beebe, Beckwith and Honig[15] who found that values of about 19.5 sq. Å. had to be assigned to krypton molecules in measurements at −195° to obtain surface area values on a variety of adsorbents in agreement with those gotten from nitrogen isotherms. This value, 19.5, is about 30% larger than one would calculate in the normal way from the extrapolated value for the density of liquid krypton at −195°.

As pointed out above, until many more data are obtained, it is impossible to say which method will, on the average, give the more reliable and more nearly correct area measurements. Meantime, it will be well to keep in mind the various points raised in the present discussion and to proceed with caution in cross-comparing areas of porous or finely divided solids obtained by the use of different adsorbates.

Summary

A correlation has been pointed out between the heat of adsorption of nitrogen and the molecular area that has to be assigned to adsorbed nitrogen molecules to bring about agreement between the method of Brunauer, Emmett and Teller and that of Harkins and Jura for measuring the surface areas of finely divided or porous solids by low temperature nitrogen adsorption isotherms. The significance, usefulness and limitations of the two methods are discussed.

PITTSBURGH, PA. RECEIVED FEBRUARY 23, 1946

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[15] Beebe, Beckwith and Honig, THIS JOURNAL, **67**, 1554 (1945).

The System Sodium Carbonate–Sodium Sulfate–Sodium Hydroxide–Water at 100°[1]

BY STANLEY J. GREEN[2] AND FRANCIS J. FRATTALI[3]

Introduction

The pilot-plant investigations by the Federal Bureau of Mines covering the extraction of alumina from Pennsylvania high-iron, diasporic, nodular clays by the lime-soda sintering process presented a problem of sulfur elimination from the plant liquors. Oxidation of the pyrite which occurs in the clays and combustion of sulfur-containing fuel produce sulfates during the sintering treatment and account for the presence of sulfate in the leach liquors. Because these liquors are recycled in the process, the sulfate concentration gradually increases and affects the efficiency of the several operations. It has been proved experimentally in the laboratory that sulfate not only detrimentally affects the amount of alumina extracted but also interferes with the recovery of soda from the processed liquors. Efficient recovery of soda is necessary in order to make this method of alumina production economical.

The plant liquors from which soda is to be re-

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[2] Formerly, Associate Chemical Engineer, Bureau of Mines, College Park, Md. Present location at Acme Coppersmithing & Machine Co., Oreland, Pa.

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