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The Adsorption of Butane on Glass Spheres

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The Brunauer–Emmett–Teller theory of multilayer adsorption has had a considerable success in supplying a foundation for interpreting adsorption data. It has also been of great practical value in providing a relatively simple and reliable method for estimating the surface area of a wide variety of finely divided materials. While the theory admirably accounts for the major features of multilayer adsorption its more detailed behavior is not entirely satisfactory. It is well known that its range of applicability extends only over a relative pressure range of about 0.05 to 0.35 and that it consistently predicts excessive adsorption in the higher relative pressure range. In the low relative pressure region the theory predicts too low an adsorption and this has been generally[1c] attributed to neglect of a varying heat of adsorption over the first layer. Further than this, however, the heat of adsorption predicted by the theory is invariably appreciably lower than that measured calorimetrically or by use of the Clapeyron equation. It was suggested by Cassie[2] that this latter difficulty might arise from a constant entropy term associated with the adsorption energy and not determinable separately from it in the theory.

In the course of some other work rather extensive data have been obtained on the adsorption of butane on glass spheres. These data were extended to cover the region of very low partial pressures in order to obtain values for the heat of adsorption at very low surface coverages. There were thus obtained adsorption data over a wide range of partial pressures, surface coverages and temperatures. It was hoped that comparison of thermodynamic quantities, experimentally obtained, with those predicted by the Brunauer–Emmett–Teller theory might provide some clue to the origin of some of the difficulties mentioned above. Of particular interest is the form of the heat of adsorption curve at low surface coverages.

The system butane–glass is very convenient for such studies. The vapor pressure of butane is such that the system is readily investigated over the rather wide temperature interval of −78 to 0°. The net heat of adsorption is sufficiently low so that (at these temperatures) very low surface coverages are easily studied. Finally, glass beads produced by fusion would be expected to provide an inert and (it was hoped) a relatively smooth surface.

Experimental

The glass spheres were made by the method of Bloomquist and Clark.[3] Electron microscope pictures showed them to be for the most part well-formed spheres with only an occasional irregularly shaped particle. With the exception of a few thread-like appendages the surface appeared perfectly smooth. This does not, of course, eliminate the possibility of surface cracks of molecular dimensions. The beads were not sized. Particles were observed with diameters ranging from a few tenths of a micron up to as high as eight microns, with the average about 3 microns.

The butane used in the experiments was obtained from a tank of C. P. *n*-butane purchased from the Ohio Chemical Company. The gas was purified by condensing it at −78° and pumping off about a third of it. The remainder was used for the adsorption measurements. The vapor pressure of the purified gas at 0° checked satisfactorily with that given by Aston.[4]

Two adsorption systems were employed. One was of conventional design for operation up to pressures of one atmosphere,[5] except that all stopcocks were replaced by mercury cut-off valves. A separate system, equipped with two McLeod gages, was used for measurements in the pressure range 0.0005 to 17.0 mm. Hg pressure. Mercury cut-offs were also used in the low-pressure system. Approximately 10 g. of the glass spheres was used in the adsorption bulb of the high pressure system and about 3 g. in the low pressure sample tube. Samples were degassed for several hours at room temperature prior to adsorption measurements. Dead space calibrations were carried out in the usual way with helium.

Temperature control was achieved through the use of appropriate low temperature baths. A stirred ice-bath was used for 0°, a mixture of solid–liquid chlorobenzene was used for −46°, and a Dry Ice–acetone bath for −78°.

Results

Figure 1 is a plot of the adsorption of nitrogen at −195° on the glass spheres, together with a BET plot, from which the surface area may be calculated.

Figures 2, 3, 4, and 5 are plots of the adsorption of butane on the glass spheres. In Fig. 6 all the data are plotted on a single graph as log p/p_0 against log v/g. Only by such a plot can the wide range of values for p/p_0 be covered in a single figure of reasonable size. Straight line BET plots are shown in Fig. 7 and in Table I are collected the areas and heat values calculated from these plots, along with the corresponding quantities obtained from the nitrogen isotherm. The straight line form of the BET equation is

$$\frac{p/p_0}{v(1 - p/p_0)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c}\, p/p_0 \qquad (1)$$

where v is the volume of gas adsorbed at pressure p, v_m is the volume of gas required to form a monolayer on the surface of the adsorbent, p_0 is the vapor pressure of the liquid adsorbate, and

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

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[1c] Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

[2] Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).

[3] Bloomquist and Clark, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 61–62 (1940).

[4] Aston and Messerly, THIS JOURNAL, **62**, 1917 (1940).

[5] Emmett, "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, 1942, pp. 1–36.

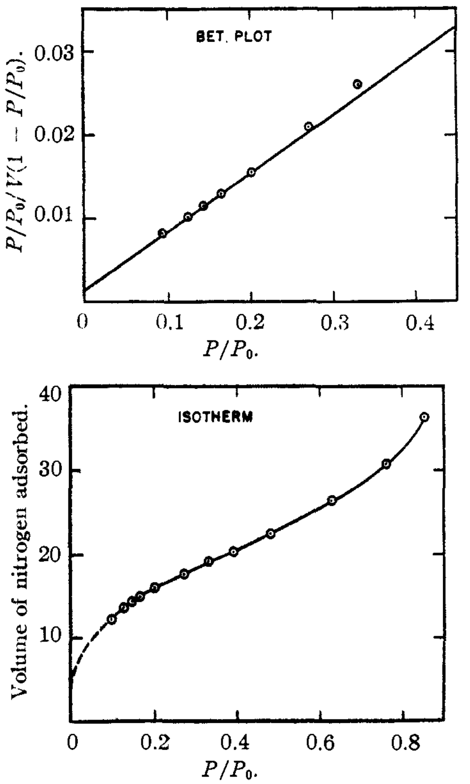

Fig. 1.—Adsorption of nitrogen on glass spheres at −195°.

The constant a_1b_2/a_2b_1 is the ratio of the evaporation–condensation coefficients for the first and higher layers. E_1 is the heat of adsorption in the first layer and E_L is the heat of condensation of the adsorbate. Areas are calculated from v_m, the volume of adsorbate corresponding to a monolayer, by obtaining cross-sectional areas for the adsorbate molecules from the liquid density and assuming hexagonal packing on the surface. For butane the value of 32 sq. Å. was used as the cross-sectional molecular area.

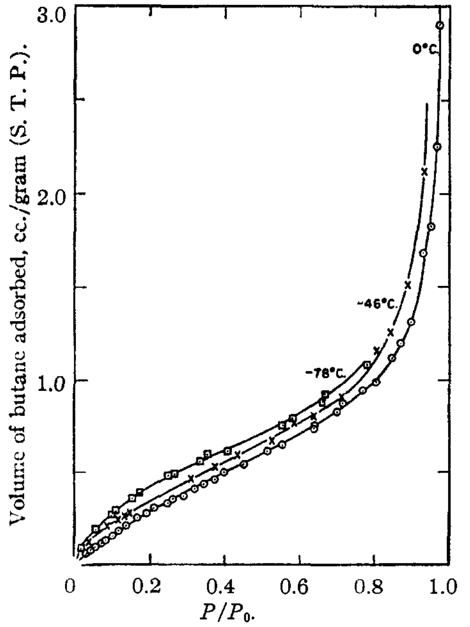

Fig. 2.—Adsorption of butane on glass spheres.

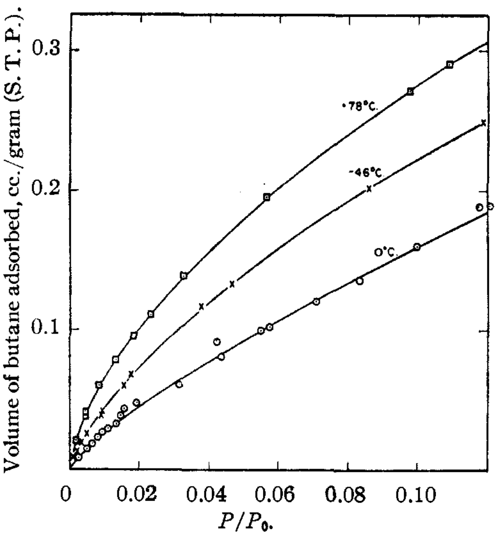

Fig. 3.—Adsorption of butane on glass spheres.

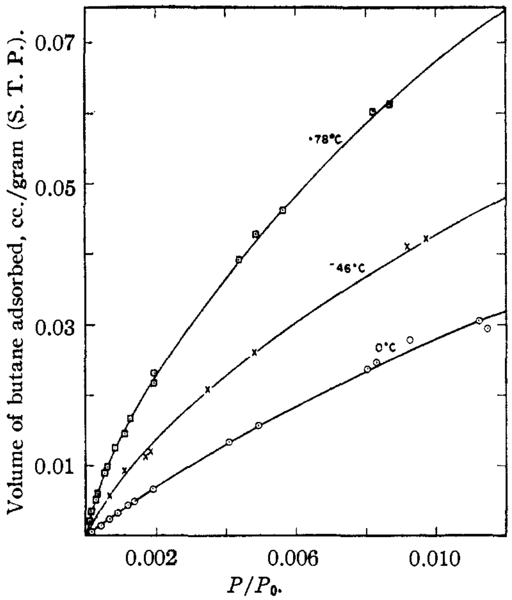

Fig. 4.—Adsorption of butane on glass spheres.

Harkins and Jura have used a method of calculating the surface area of various non-porous solids[6] which involves plotting the adsorption data according to the equation

$$\log \frac{p}{p_0} = B + \frac{A}{v^2} \qquad (2)$$

where A and B are constants. The square root of the slope of the straight line is proportional to the surface area. The proportionality constant was determined empirically for several gases by cali-

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[6] Harkins and Jura, This Journal, 66, 1366 (1944).

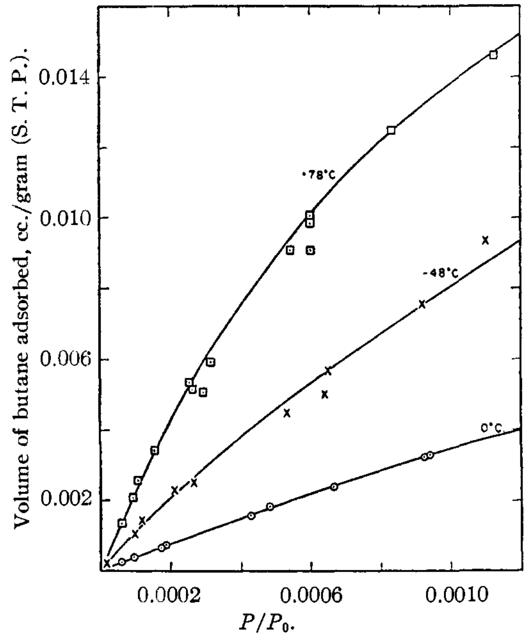

Fig. 5.—Adsorption of butane on glass spheres.

bration against an absolute determination of the area.[7] The factor for butane at 0° is 13.6, which corresponds to a cross-sectional area for butane of 56.6 sq. Å. The butane data are plotted in this fashion in Fig. 8. Below relative pressures of 0.3 to 0.4 the plots are distinctly curves, but points in the higher pressure ranges yield reasonably straight lines from which areas may be calculated. The areas calculated using the Harkins and Jura method are given in Table I. The derivation of the Harkins and Jura equations involves a transformation through the Gibbs adsorption equation. This transformation inserts the absolute temperature in the denominator of the term involving $1/v^2$. It would be therefore expected that the constant relating the slope of the plot to the surface area, would vary inversely as the square root of the absolute temperature. For the figures in parentheses in Table I, it has been assumed that the constant 13.6 applies only to 0° and areas for −46° and −78° have been calculated assuming the constant varies as $1/\sqrt{T}$. The correction appears to be in the right direction and of approximately the right size since it yields fairly consistent area values for all three temperatures.

TABLE I

SURFACE AREA OF GLASS SPHERES

Gas	Temperature, °C.	c	Area, sq. m./g. by BET[a] method	Area, sq. m./g. by H. and J. method
C_4H_{10}	− 78	11.55	3.56	5.36[b] (4.51)
C_4H_{10}	− 46	8.47	3.34	4.81[b] (4.37)
C_4H_{10}	0	5.40	3.35	4.69[b] (4.69)
N_2	−195	55	5.82	4.47 ..

[a] Corrected for temperature variation of density of liquid butane. Cross-sectional area at 0° assumed to be 32 ss. Å. [b] Calculated using factor of 13.6 for all temperatures. Figures in parentheses calculated assuming factor is 13.6 for 0° and varies inversely with square root of absolute temperature. The factor 13.6 is equivalent to a cross-sectional area of 56.6 Å.[2]

Thermodynamic Data.—The Clausius–Clapeyron equation is used for calculating the heat of adsorption. For convenience the equation was used in the form

$$\log\left(\frac{p}{p_0}\right)_2 - \log\left(\frac{p}{p_0}\right)_1 = \frac{-\Delta H_R}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad (3)$$

where $(p/p_0)_2$ is the relative pressure for a given value of volume adsorbed at T_2, $(p/p_0)_1$ that at T_1, and ΔH_R is the heat of adsorption referred to normal liquid. This equation directly incorporates the heat of liquefaction of the adsorbate, and the heats thus calculated are therefore not absolute but relative to the heat of liquefaction of normal liquid. Figure 6 provides a very easy way

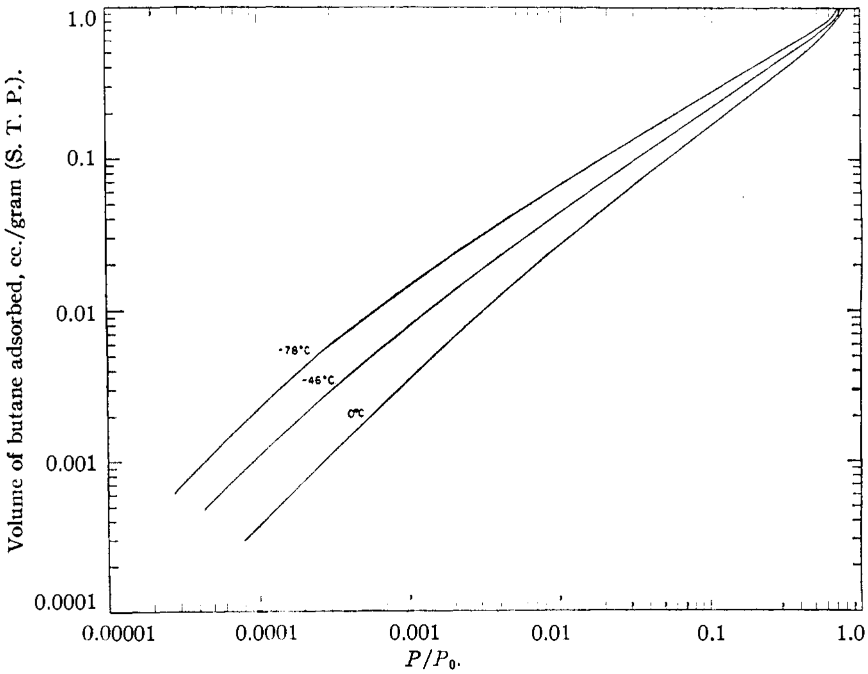

Fig. 6.—Adsorption of butane on glass spheres.

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[7] Harkins and Jura, THIS JOURNAL, **66**, 1362 (1944).

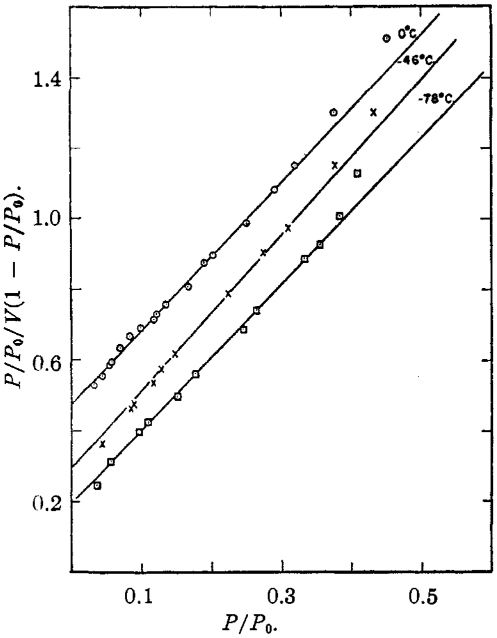

Fig. 7.—Adsorption of butane on glass spheres, B. E. T. plot.

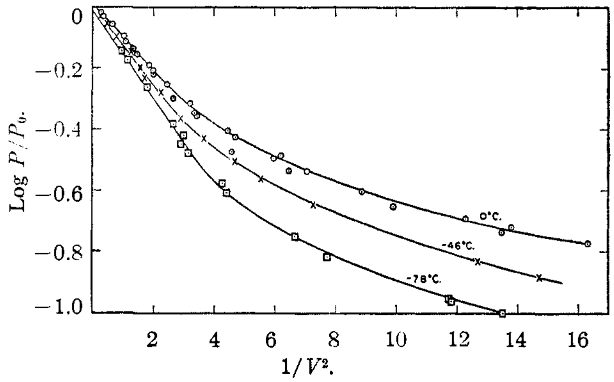

Fig. 8.—Adsorption of butane on glass spheres, Harkins and Jura plot.

of graphically carrying out these calculations. The heat of adsorption, ΔH_R, is directly proportional to log $(p/p_0)_2$ − log $(p/p_0)_1$. In Fig. 6 this quantity is proportional to the horizontal distance between any two isotherms at a given value of v. This distance then, multiplied by a factor determined by $2.303RT_1T_2/(T_2 - T_1)$ and the length of the logarithmic cycle, immediately gives the desired heat of adsorption. The heat values were obtained in this way from a large logarithmic plot of the data. The values thus obtained are shown in Fig. 9 on a logarithmic plot to spread out the values in the region of low p/p_0. The cross-hatching indicates the estimated limits of error. The tendency to constant values in the very low range will be noted. For comparison with these experimentally determined values, the heats of adsorption have been calculated from the BET equation with the appropriate values of c and v_m. The integral energy of adsorption, ΔE_I, relative to the energy of normal condensation is

$$[\Delta E_I = (E_1 - E_L)v_1] \qquad (4)$$

where E_1 is the molal energy of adsorption in the first layer, E_L the molal energy of liquefaction of normal liquid and v_1 is the number of moles of adsorbate in the first layer at the relative pressure at which the integral heat is desired. Differentiation of equation (4) with respect to V, the total number of moles of adsorbate, gives $\Delta E_R = (E_1 - E_L)\mathrm{d}v_1/\mathrm{d}V$, the differential molal energy of adsorption relative to normal liquid as a function of the total amount of gas adsorbed. This value should be directly comparable to ΔH_R determined experimentally since we are dealing with condensed phases throughout and there should be no difference between ΔH and ΔE. The quantity $E_1 - E_L$ was obtained in the usual way from the c value of the BET plots and $\mathrm{d}v_1/\mathrm{d}V$ was obtained by differentiation of the expression given by Hill[8] for the number of moles of adsorbate in the first layer as a function of total amount adsorbed. The experimental and calculated curves for the heat of adsorption are compared in Fig. 10.

The free energy change in going from condensed liquid having a vapor pressure p_0 to the adsorbed phase having a vapor pressure p, is given by $\Delta F = RT \ln p/p_0$. Free energy of adsorption values were thus calculated directly from the data and also from the BET equation. Of course, over the range of applicability of the BET equation, the experimental and calculated free energies must agree. From these free energy values and the corresponding heat values previously determined, entropies of adsorption, experimental and theoretical, were calculated through the relation $\Delta S = (\Delta H - \Delta F)/T$. Experimental and theoretical entropy values are compared in Fig. 11.

If values for c in the BET equation are available over a temperature range it becomes possible to determine separately the quantities a_1b_2/a_2b_1 and $E_1 - E_L$. Since

$$c = \frac{a_1b_2}{a_2b_1} e^{\frac{E_1 - E_L}{RT}}$$

a plot of log c against $1/T$ should be a straight line (assuming $E_1 - E_L$ is not strongly dependent on temperature). The slope of this plot serves for the evaluation of $E_1 - E_L$ and the intercept for

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[8] T. L. Hill, *J. Chem. Phys.*, **14**, 268 (1946). Hill showed that the BET derivation leads to the conclusion that the number of moles of gas V_1 adsorbed in the first layer is given by the equation

$$\frac{V_1}{V_m} = \frac{c(V/V_m + 1) - [(1 - V/V_m)^2c^2 + 4V/V_mc]^{1/2}}{2(c - 1)} \qquad (5)$$

where the symbols are the molal equivalents of those used in equation (1). Differentiation with respect to the total number of moles of gas adsorbed gives

$$\frac{\mathrm{d}V_1}{\mathrm{d}V} = \frac{c}{2(c - 1)}\left\{1 - \frac{V/V_m - 1 + 2/c}{[(1 - V/V_m)^24/cV/V_m]^{1/2}}\right\} \qquad (6)$$

Equations (4) and (6) were used to calculate the differential heats of adsorption that one would expect from the BET theory.

that of a_1b_2/a_2b_1. Such a plot for the butane on glass data is shown in Fig. 12. Values of $E_1 - E_L$ and a_1b_2/a_2b_1 determined from this plot are listed in Table II. The range of values shown indicates the outside limits obtainable from different straight lines through the three points, which are not quite in a straight line. Evidently the ratio a_1b_2/a_2b_1 is essentially unity and the slope of the plot yields a value for $E_1 - E_L$ in reasonable agreement with those obtained in the usual way from the individual c values.

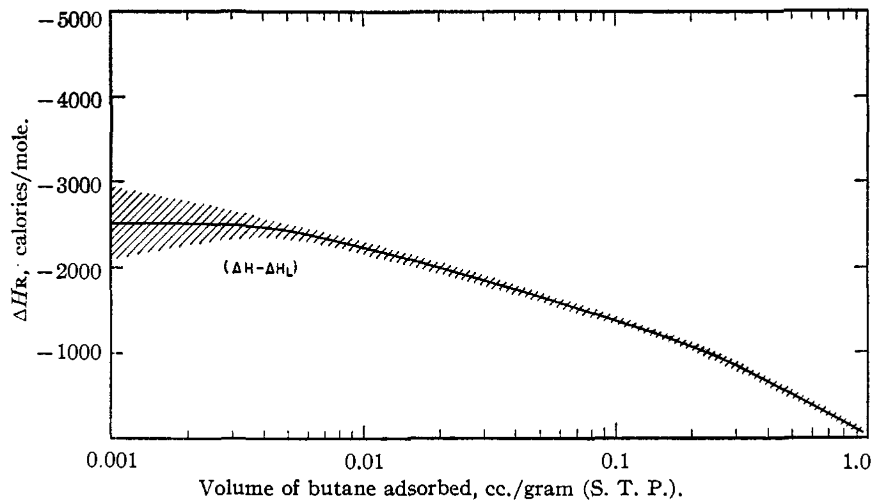

Fig. 9.—Adsorption of butane on glass spheres and heat of adsorption.

TABLE II

CALCULATION FROM "c" VALUES

($E_1 - E_L$) from "c" values assuming a_1b_2/a_2b_1 is unity	−78°	947 calories/mole
	−46°	962 calories/mole
	0°	962 calories/mole
($E_1 - E_L$) from slope of plot of log "c" vs. $1/T$	881 to 1165 calories/mole Mean = 1015 calories/mole	
a_1b_2/a_2b_1 from intercept of plot of log "c" vs. $1/T$	0.7 to 1.2	

Discussion

The system is quite normal in its behavior, and when viewed from the point of view of its pressure–volume adsorbed relations, requires little comment. The BET method for determining surface areas leads, as usual, to considerably lower surface area values, when the calculations are based on the butane isotherm than when they are based on the nitrogen isotherm, provided the values 32 and 16.2 Å.^{2} are used for the cross-sectional areas of the molecules of butane and nitrogen, respectively. With a smooth glass adsorbing surface it does not seem reasonable to assign this discrepancy to a screening out of the larger butane molecules from small holes. It must be that butane occupies a larger area on the surface than would be calculated from the liquid density. In calculating the area values recorded in Table I, corrections for the thermal expansion of the liquid were applied.

In the Harkins and Jura plots there is no straight line relation between the logarithm of the relative pressure and the reciprocal square of the volume adsorbed, as required in their theory, if the data in the relative pressure range 0.05 to 0.35, which is the region of usual validity of the BET equation, is used. For relative pressures above 0.3–0.4, however, the plots are relatively good straight lines and a reliable slope can be determined. The values for the areas thus determined are seen, from Table I, to be quite reasonable. It is interesting that the temperature correction demanded by the theory seems to operate in the right direction and to approximately the right extent. The factor 13.6 is equivalent to assuming a cross-sectional area for butane of about 56.6 Å.^{2} rather than the 32 Å.^{2} calculated from the liquid density and usually used in the application of the BET

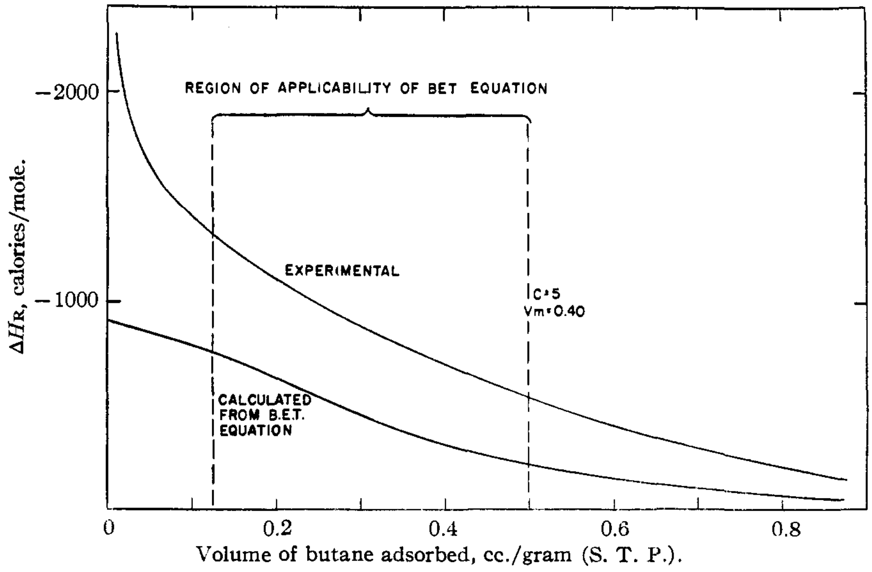

Fig. 10.—Adsorption of butane on glass spheres and heat of adsorption.

method. If a cross-sectional area of 56.6 Å.^{2} is used for butane in applying the BET method to the present work, good agreement with the nitrogen area is obtained but, as will be seen from Table I, the Harkins and Jura factor of 13.6 gives areas about 25% too low compared to the BET nitrogen area. The reason for this is readily seen to be that the BET and Harkins and Jura nitrogen areas do not agree. Nitrogen adsorption on glass beads has a low "c" value (55) and this constitutes a case wherein the nitrogen values for the two methods do not agree.[9] It will be noted from the table that there is good agreement between the area values calculated from butane and nitrogen data if the Harkins and Jura method and constants are used for both. Of course this should not be surprising since the constants were empirically determined to give such agreement. As has already been pointed out, equally good agreement could be obtained between the two gases using the BET method if a comparable procedure is used and the cross-sectional area of butane is chosen to give agreement with the nitrogen area. At the moment there seems to be no basis for making a choice between the BET method and the Harkins and Jura method for obtaining areas, if the Harkins and Jura method is applicable and yields a single straight line. The BET method when used to obtain absolute surface areas involves the assumption that the cross-sectional area of a molecule is independent of the substrate; the Harkins and Jura method assumes the same for its empirically chosen conversion factor. Probably such an assumption is not strictly justified for either method. Perhaps the best that can be done at the present is to admit that absolute areas cannot be relied on to better than 20–30% and regard both methods as adequate within these limits.

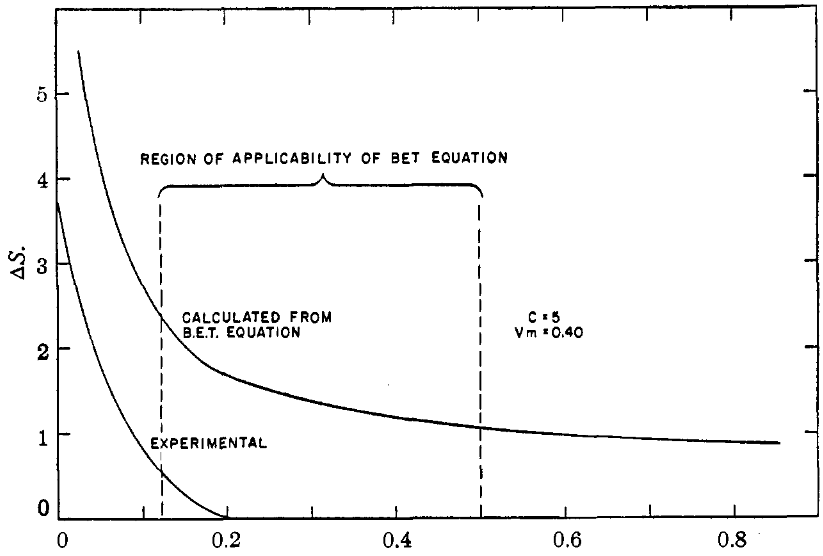

Fig. 11.—Adsorption of butane on glass spheres and entropy of adsorption.

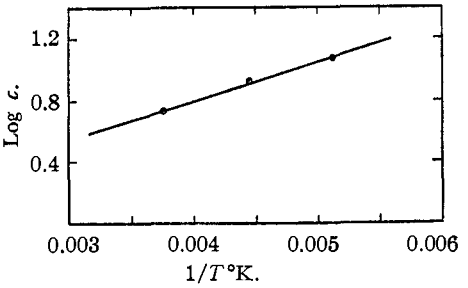

Fig. 12.—Adsorption of butane on glass spheres—variation of "c" of B. E. T. equation with temperature.

Thermodynamics.—The form of the heat curve is interesting, particularly at low surface coverages. Below about one per cent. coverage the heat appears to be constant at a rather high value. Beyond this it drops off at least approximately logarithmically with increasing adsorption. There is some uncertainty in the data in the low ranges; an unmistakeable departure, however, from its behavior at higher coverages occurs in this region. This is best illustrated by the logarithmic plot of Fig. 6 which spreads out the data at low partial pressures. It is also reflected in the nearly parallel straight line portions of the isotherms at the left in Fig. 6. Clausius–Clapeyron computations from parallel straight lines in this type of plot, of course, lead to constant heat values.

The sharp drop-off in the heat after about one per cent. of the surface is covered is difficult to explain. Roberts and Orr[10] and Orr[11] have made extensive theoretical calculations on the heat of adsorption of argon on alkali halide crystals and on the variation of the heat with amount adsorbed. Orr[12] determined the heats experimentally for the adsorption of oxygen, nitrogen and argon on potassium chloride and cesium iodide. Lateral van der Waals interaction invariably (as would be expected) contributes only in a way to increase the heat with surface coverage; only in the case of adsorption on the cesium positive ion faces of the crystal was there an electrostatic repulsive energy, arising from the oriented induced dipoles of the adsorbed atoms, sufficiently large to balance out the van der Waals attractive forces and give a net decrease in the energy of adsorption with increas-

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[9] P. H. Emmett, This Journal, **68**, 1784 (1946).

[10] Roberts and Orr, *Trans. Faraday Soc.*, **34**, 1346 (1938).

[11] Orr, *ibid.*, **35**, 1247 (1939).

[12] Orr, *Proc. Royal Soc.* (*London*), **A173**, 349 (1939).

ing coverage. In general, except for regions of very low coverage, agreement between experiment and theory was quite good. It is quite improbable that induced dipoles in butane adsorbed on glass could account for the observed decrease in heat of adsorption; indeed, the decrease in heats starts at such low surface coverages that no kind of lateral interaction would be expected to come into play. Frankenburg, in his study[13] of the adsorption of hydrogen on tungsten at elevated temperatures and also one of the authors (Davis) in the study of nitrogen adsorption on tungsten[13a] found the same behavior of the heat of adsorption at low surface coverages. Indeed, the behavior of the butane–glass system is so similar to that of the hydrogen–tungsten system that one is led to suspect the presence of something fundamentally general. In an attempt to account for the decreasing heat of adsorption, Frankenburg postulated a repulsive force operating between adsorbed atoms even at high dilutions that had its origin in the electron cloud that was assumed to exist in the substrate metal in the neighborhood of each adsorbed atom. No such device can be appealed to in the case of the butane–glass system, yet the experimental similarity of the data in the two cases tempts one to seek a common explanation. It does not seem probable that it will be found in the existence of lateral repulsive forces. Perhaps one is forced to the view that a heterogeneous set of adsorption sites is responsible. If so, the distribution of such sites must be of a remarkably universal form.

Reference to Figs. 10 and 11 makes it immediately apparent that the BET equation does not do too well in predicting individually the heat and entropy of adsorption. Although the form of the calculated heat curve approximates that of the experimental curve, it is everywhere much too low. Since the equation fits the data, and therefore the experimental and calculated free energies must agree, at least over the range of applicability, the entropy is everywhere correspondingly high. Experimentally, the entropy contribution has almost disappeared before a monolayer is completed and the heat contribution accounts for the free energy of adsorption thereafter. In the case of the BET equation the heat soon drops to a rather low value and the entropy continues to make an appreciable contribution to the adsorption free energy. It looks as though the theory incorporates too large an entropy contribution: this may be the origin of the excessive adsorption predicted by the theory for higher layers. A further indication of some basic difficulty is the recognized fact that the value for $E_1 - E_L$ obtained from the c value of the BET equation is so much smaller than the Clausius–Clapeyron heat. This cannot be blamed on a deviation of the factor a_1b_2/a_2b_1 from unity, at least in the present case, since it has been independently determined to be essentially unity. Even more disturbing is the result of plotting log c against $1/T$ for some other data. If the data of McGavack and Patrick[14] for the adsorption of sulfur dioxide on silica gel is thus plotted, the constant a_1b_2/a_2b_1 turns out to be about 6 and $E_1 - E_L$ about 700 calories instead of around 1700 as obtained directly from the c value. Several sets of data for the adsorption of nitrogen[15] at low temperature yield an average value of about 10 for a_1b_2/a_2b_1 and a value of about 400 calories for $E_1 - E_L$. Normally $E_1 - E_L$ determined from the c values for low temperature nitrogen adsorption is in the neighborhood of 700–800 calories. Thus in these cases, separate evaluation of a_1b_2/a_2b_1 has made agreement between $E_1 - E_L$ and the measured heat of adsorption considerably worse, rather than better.

Just wherein improvements are to be made to the simple BET theory is not clear. One obvious thing to do would be to attempt to take molecular interactions into account. Such a refinement has been approached by Hill.[16] The resulting equations are quite complicated and no application to experimental data has yet been published. As adsorption data accumulate, deficiencies in the simple theory become more apparent and the need for satisfactory refinements grows. The BET theory is theoretically sound and improvements will probably come through the use of an improved adsorption model and the incorporation of hitherto consciously ignored factors.

Summary

Data for the adsorption of butane on glass spheres has been reported for a relative pressure range from below 0.0001 up to near saturation at temperatures of −78, −46 and 0°. From these data heats of adsorption have been calculated through the Clausius–Clapeyron equation. The heat of adsorption tends to remain constant up to several per cent. surface coverage after which it decreases approximately logarithmically with increasing adsorption. Experimental heats and entropies of adsorption have been compared with the corresponding quantities calculated from the BET equation. The theory was found somewhat deficient in its ability to predict individually these thermodynamic functions. A plot of log c against $1/T$ was used for the independent evaluation of $E_1 - E_L$ and the coefficient a_1b_2/a_2b_1 in the expression for the constant c of the BET theory. In the case of butane on glass, a_1b_2/a_2b_1 was essentially unity. Some other data were thus treated and a_1b_2/a_2b_1 found to be larger than unity and $E_1 - E_L$ correspondingly lower than usual.

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[13] Frankenburg, THIS JOURNAL, **66**, 1827 (1944); **66**, 1838 (1944).

[13a] Davis, *ibid.*, **68**, 1395 (1946).

[14] McGavack and Patrick, *ibid.*, **42**, 946 (1920).

[15] Brunauer and Emmett, *ibid.*, **60**, 309 (1938).

[16] Hill, Presented at the Symposium on the Adsorption of Gases, Colloid Division, 110th meeting of the American Chemical Society, Chicago, Ill., September, 1946.