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## Differential Heats of Adsorption of Nitrogen on Carbon Blacks

BY L. G. JOYNER AND P. H. EMMETT

It has long been realized that measurements of the heat evolved during the physical adsorption of gases upon solids might yield considerable information concerning the nature of the solid surface. Of particular interest would be the variations of the differential heat with the amount of gas adsorbed.

Unfortunately, very little accurate work has been done by either the calorimetric or the isosteric method for measuring heats of adsorption and few attempts have been made to compare the two methods. Such attempts as have been made have been well summarized and discussed by Brunauer.<sup>1</sup>

In recent years calorimetric technique has been so improved, especially by Beebe<sup>2</sup> and his co-workers, that it is possible to detect variations in the differential heat of adsorption which are smaller than the experimental error involved in much of the early work in the field. More precise methods for measuring the adsorption of gases on solids have also been developed. In view of the fact that calorimetric measurements such as Beebe's are rather complicated and time consuming, it seemed worthwhile to ascertain whether the simpler isosteric method for measuring the heat of adsorption was capable of detecting the same details of the heat curve as the calorimetric method. To this end, we have carried out and are here reporting detailed adsorption studies of nitrogen on portions of the same samples of carbon black for which Beebe, Biscoe, Smith and Wendell<sup>2a</sup> have recently reported the most complete calorimetric measurements of the heat of adsorption of nitrogen that have so far been published. The samples were kindly given to us by Dr. Beebe.

## Experimental

**Materials.**—Two carbon blacks were selected for the present investigation. These were the same samples used by Beebe, Biscoe, Smith and Wendell<sup>2a</sup> and have been described in detail in their paper. The two carbon blacks were Spheron Grade 6 and Graphon. The Spheron Grade 6 is a medium processing channel black (MPC). Graphon is a partially "graphitized" carbon black formed by heating MPC black to 3200°.

The nitrogen adsorbate was Airco Prepurified nitrogen. It was merely dried in a liquid nitrogen trap prior to being used.

**Apparatus.**—The adsorption apparatus was a modified version of the type described by Emmett.<sup>3</sup> Pressures above 1 cm. were determined to 0.1 mm. on a 10-mm.

bore manometer with a vernier reader. Lower pressure determinations were made on a special manometer read by means of a microscope cathetometer. This was similar to the system described by Harkins and Jura.<sup>4</sup> The precision of these low-pressure readings was about 0.01 mm. The normal vapor pressure of nitrogen ( $P_0$ ) was determined continuously and directly by means of a separate manometer and bulb partially filled with liquid nitrogen and placed in the low-temperature bath in close proximity to the adsorption bulb.

The adsorption isotherms at -183 and -195° were made using a liquid oxygen and a liquid nitrogen bath, respectively. The isotherms at -205° were made in a specially designed, low temperature system, details of which will be published in the near future. Briefly, the lower temperature was obtained by decreasing the pressure over liquid nitrogen. By means of a vapor pressure controller, relay and pump, the pressure was kept constant to within a few tenths of a mm. The total temperature variation over an entire run was less than 0.1°.

All surface area values were obtained by a linear plot of the adsorption data according to the Brunauer, Emmet and Teller (B.E.T.) equation<sup>5,6</sup>

$$\frac{x}{V(1-x)} = \frac{1}{V_m C} + \frac{(C-1)x}{V_m C} \quad (1)$$

where  $x$  is the relative pressure at which the volume  $V$  of gas (S.T.P.) is adsorbed,  $V_m$  is the volume of gas required to form a monolayer and  $C$  is a constant proportional to  $\exp. (E_1 - E_L)/RT$ .  $E_1$  is defined<sup>5</sup> as the "average heat of adsorption for the first layer" and  $E_L$  the heat of liquefaction of the adsorbate.<sup>7</sup>

## Results

Figure 1 shows the nitrogen adsorption isotherms for Grade 6 Spheron at -183.1° and -194.6°. Similar isotherms for Graphon at -182.8°, -194.8° and -204.7° are shown in Fig. 2. In Fig. 3 the low pressure regions of the Graphon isotherms are given in more detail. All of the isotherms are actually composites of several separate runs. Many more points were taken

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

(5) Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

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

(7) It must be kept in mind that  $E_1$  does not and should not necessarily agree with direct experimental values for the heat of adsorption in the first layer.<sup>2a</sup> To begin with,  $E_1$  is evaluated from plotting adsorption data by equation 1 for relative pressures ranging from 0.05 to about 0.3. Accordingly, the  $E_1$  as deduced from the constant  $C$  in equation 1 is more nearly the average heat of adsorption for the less active part<sup>5</sup> of the surface since most of the first layer would have been completed already at a relative pressure of 0.05 for many adsorbates. Furthermore, since  $C$  is defined as

$$\frac{a_1 b_2}{a_2 b_1} \exp. (E_1 - E_L)/RT$$

it is possible to obtain  $E_1$  from  $C$  only by evaluating the term  $a_1 b_2 / a_2 b_1$ . Actually this term is frequently assumed equal to unity though recent calculations<sup>8,9</sup> suggest that it may differ from unity by a factor of 10 to 100. Accordingly, equation 1 can be expected to yield only an approximate value for  $E_1$  and at best gives an  $E_1$  characteristic of the less active parts of the surface.

(8) Emmett, *THIS JOURNAL*, **68**, 1784 (1946).

(1) Brunauer, "The Adsorption of Gases and Vapors—Physical Adsorption," Princeton Press, Princeton, N. J., 1943, Chapter 8.

(2) (a) Beebe, Biscoe, Smith and Wendell, *THIS JOURNAL*, **69**, 95 (1947). (b) Beebe and Orfield, *ibid.*, **59**, 1627 (1937). (c) Beebe and Dowden, *ibid.*, **60**, 2912 (1938). (d) Beebe and Stevens, *ibid.*, **62**, 2134 (1940).

(3) P. H. Emmett, "American Society for Testing Materials, Symposium on New Methods for Particle Size Determination," 1941, p. 95.

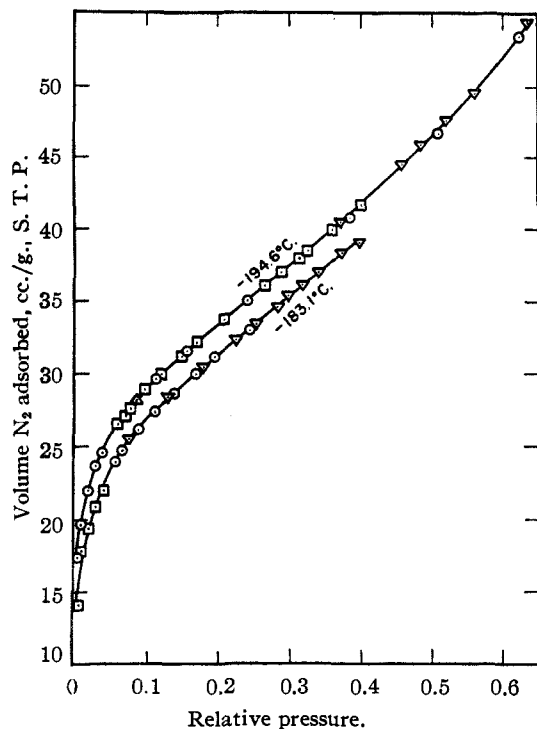


Fig. 1.—Adsorption of nitrogen on Grade 6 Spheron at  $-183.1$  and  $-194.6^{\circ}$ .

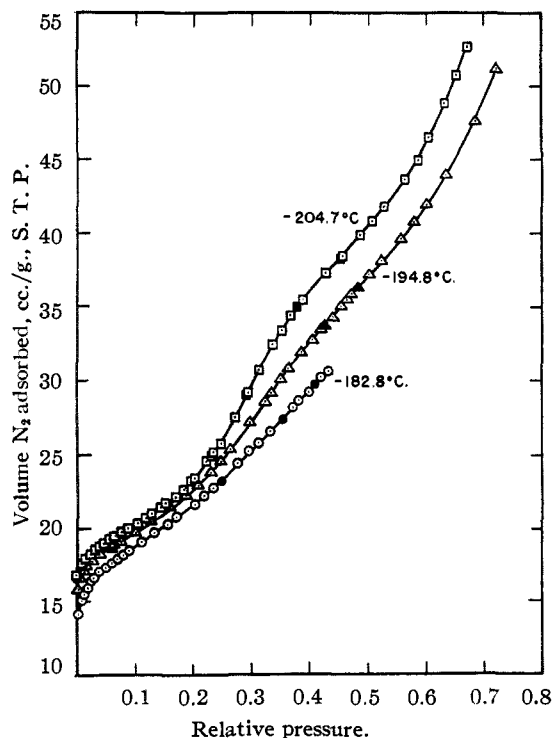


Fig. 2.—Adsorption of nitrogen on Graphon at  $-182.8$ ,  $-194.8$  and  $-204.7^{\circ}$ . Solid symbols are desorption points.

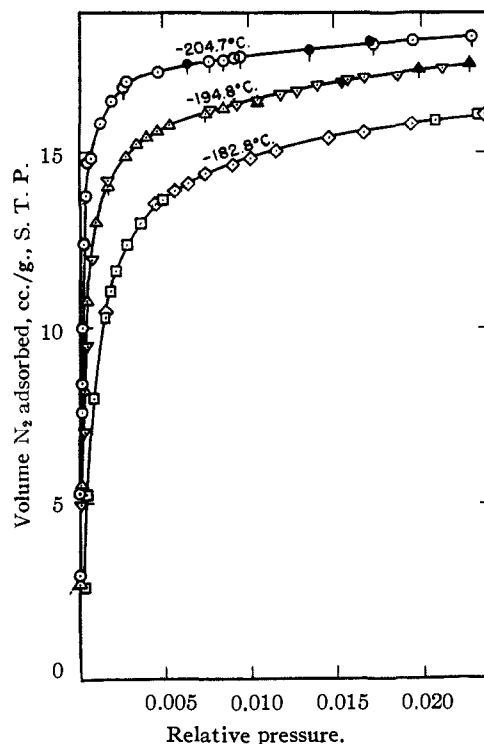


Fig. 3.—Low pressure detail of the adsorption of nitrogen on Graphon at  $-182.8$ ,  $-194.8$  and  $-204.7^{\circ}$ . Different symbols represent separate runs. Solid symbols are desorption points.

than are shown.<sup>9</sup> Those given in the figures, however, are representative and serve to illustrate the precision of the measurements. Separate runs are indicated by the different symbols in Fig. 3. The  $-183^{\circ}$  isotherms could not be carried above a relative pressure of about 0.4 because of the limitations of the apparatus. That the carbon blacks are probably non-porous is indicated by the superposition of the desorption points on the adsorption curve in the region above 0.4 relative pressure, this being the region in which hysteresis usually occurs for porous substances. The desorption points were taken after the maximum volume of gas shown by the curves in Fig. 2 had been adsorbed.

### Calculations and Discussion

**Calculation of the Heat of Adsorption.**—The differential heat of adsorption was calculated from the Clausius-Clapeyron equation in the form<sup>10</sup>

(9) For additional data order Document 2530 from American Documentation Institute, 1719 N St., N. W., Washington 7, D. C., remitting 50¢ for microfilm or 50¢ for photoprints.

(10) Wilkins, *Proc. Roy. Soc. (London)*, **A164**, 496 (1938), has suggested that the correct method of applying the Clausius-Clapeyron equation to adsorption data entails the use of a constant fraction of the surface covered rather than a constant volume of adsorbed gas at the several temperatures being used. If such calculations are made for the data in the present paper for constant values of  $V/V_m$  ( $V_m$  varying with temperature as indicated in column 3 Table I) the resulting  $\Delta H$  value is smaller in absolute value than the curves

$$\Delta H = 2.303R \left( \frac{T_1 T_2}{T_2 - T_1} \right) (\log P_2 - \log P_1)_{\text{const. } V} \quad (2)$$

For each isotherm  $\log P$  was plotted against the volume of gas adsorbed,  $V$ . Figure 4 shows this plot for the three isotherms on Graphon. The vertical distance between the lines was measured at a given value of  $V$  and inserted into Equation 2;  $\Delta H$  for various given values of  $V$  was then calculated.

In Figure 5 are plotted as a function of  $V/V_m$  the differential heat of adsorption for nitrogen on Spheron measured isothermally as above (solid line) and the calorimetric results for the same system (symbols) as measured by Beebe and his co-workers.<sup>2a</sup> Figure 6 shows a similar comparison for the nitrogen-Graphon system.

Since Equation 2 is very sensitive to small variations in the pressure, especially in the low pressure region, vertical lines are used in Figs. 5 and 6 to indicate the maximum variation observed. The extent of this variation in terms of pressure is indicated by the envelope lines for the  $-194.8^\circ$  curve in Fig. 4. Variations of only 0.01 to 0.02 mm. in the low pressure region have a considerable effect upon the calculated heat value, whereas at higher pressures even larger variations have negligible effect.

**Changes in  $\Delta H$ ,  $\Delta F$  and  $\Delta S$  during the Adsorption of Nitrogen on Carbon Blacks.**—It is apparent from Figs. 5 and 6 that the agreement between the differential heats of adsorption as calculated from the isotherms by Equation 2 and those determined calorimetrically by Beebe<sup>2a</sup> is remarkably good. The isosteric heats of adsorption of nitrogen on the Graphon sample are of better precision than those on Grade 6 Spheron, due to an improvement of the apparatus. It is doubtful, however, that this lower precision for the Spheron data can account for the rather large discrepancy observed for Spheron in the region of the monolayer between the isosteric heats and the portion of the calorimetric heats represented by the closed circles. It may be noted

shown in Figs. 5 and 6 by 100 to 400 calories. However, the justification of this proposed method of applying the Clausius-Clapeyron equation is not clear at the present writing. Certainly the two papers of Wilkins (also Wilkins, *Proc. Roy. Soc. (London)*, **A164**, 510 (1938)) dealing with the subject appear to be so full of misprints as to be unsuitable as a theoretical guide to the problem. Our own data show definitely that any heat of adsorption values calculated on the basis of constant fraction of the surface covered will be smaller than those calculated by equation 2 with volume of adsorbed gas constant. Wilkins' theoretical treatment led to what seems to be an erroneous conclusion that the heat of adsorption is larger if calculated by constant fraction of the surface covered than by constant volume.

that the calorimetric data represented by the open circles and triangles are much closer to the isosteric line in this region than are points shown as closed circles.

For the adsorption of nitrogen on Graphon the agreement between the isosteric and calorimetric

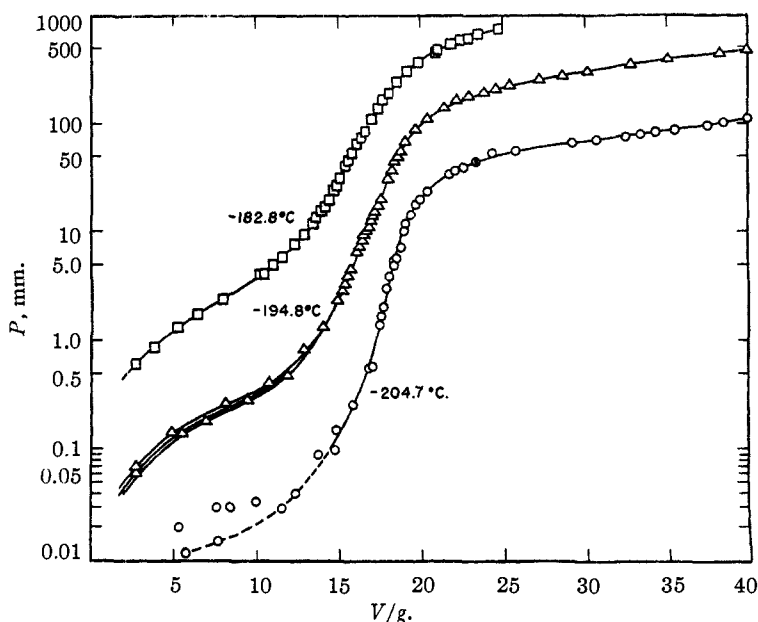


Fig. 4.—Logarithmic plot of the Graphon isotherms for purposes of calculating the differential heat of adsorption, showing the experimental deviations at extreme low pressures.

heats is especially good. The isosteric data reproduce faithfully the rather unusual calorimetric curve. Since for this system the isotherm was determined at three temperatures, there are three possible ways of calculating the differential heats by Equation 2. The various results are indicated in the figure by separate symbols. Above 0.7 monolayer the heats calculated from all three pairs of isotherms agree very well. Below 0.7 monolayer the  $-204.7^\circ$  isotherm involves a larger possible error because of the low absolute pressure and cannot be used to calculate an isosteric heat with accuracy. It is not surprising, therefore, that the heat values calculated from the  $-204.7^\circ$  and the  $-182.8^\circ$  isotherms and shown by open triangles are in poor agreement with the other isosteric and with the calorimetric values.

The isotherms of the Graphon system shown in Fig. 2 all have an unusual hump starting at a relative pressure of about 0.2. This hump was also obtained but not discussed by Beebe<sup>2a</sup> and is not directly associated with the large rise in the differential heat curve since the latter occurs at 0.75 monolayer while the isotherm hump is much higher. There is, however, a much smaller rise in the heat curve at 1.75 monolayers which is associated with the isotherm hump. It is remarkable that the second and smaller rise in the differential

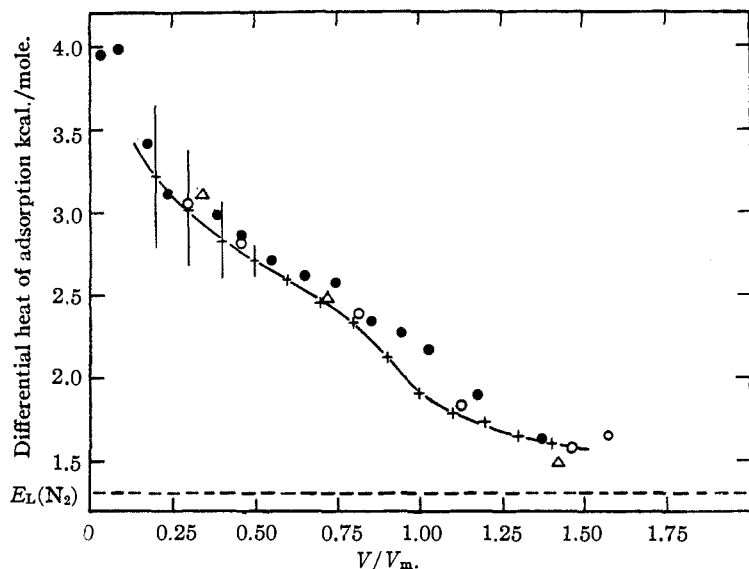
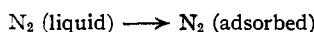


Fig. 5.—Differential heats of adsorption for nitrogen on Grade 6 Spheron as determined calorimetrically by Beebe, Biscoe, Smith and Wendell,<sup>2a</sup> (O, ●, Δ), and isothermally by the authors (+). The length of the vertical lines represents the total spread of the values calculated from the isothermic data.

heat curve is almost exactly one monolayer separated from the larger rise. It would almost seem that whatever forces cause the first rise are carried through and repeated in the second layer.

If one considers the process



it is a simple matter to calculate from the foregoing data the change in heat content, ( $\Delta H$ ); the free energy change, ( $\Delta F$ ); and the entropy change, ( $\Delta S$ ).  $\Delta H$  is simply the difference between the differential heat of adsorption and the heat of liquefaction.  $\Delta F$  is given by

$$\Delta F = RT \ln P/P_0 \quad (5)$$

The free energy change so calculated was found to be independent of the temperature at least over the range of temperature studied. The entropy change is then obtained from the relation  $T\Delta S = \Delta H - \Delta F$ .

Figures 7 and 8 show how these properties vary with  $V/V_m$  for the two carbon blacks studied. Although the portion of the  $\Delta S$  curve for Spheron below a  $V/V_m$  value of 0.5 is quantitatively questionable,  $\Delta S$  undoubtedly remains negative down to at least a value of  $V/V_m$  equal to 0.2. For Graphon, the value of  $\Delta S$  is positive up to a  $V/V_m$  value of 0.3 and again for a  $V/V_m$  value between 1.0 and 1.5.

Beebe and his co-workers<sup>2a</sup> have pointed out that on the basis of calculations by Barrer<sup>11</sup> the observed decrease in the heats for the Spheron with the amount of surface coverage cannot be accounted for by interaction between adsorbed molecules. However, as they point out, it is possible that such interaction forces may account for the increase in heats over the  $V/V_m$  range between 0.5 and 1.0 in the case of Graphon.

If one accepts Beebe's<sup>2a</sup> suggestion that the heat treatment to which Spheron is subjected when it is converted to Graphon eliminates most of the highly active centers found on the Spheron a possible explanation of the entropy curves is suggested. In the case of the Spheron where active points are present, the adsorbed phase is more or less ordered with a resulting negative entropy change over the entire course of the adsorption. In the Graphon system the first molecules are adsorbed in a very random or disordered manner giving rise to the positive portion of the entropy curve. Once the surface is partially covered, interaction forces, such as those

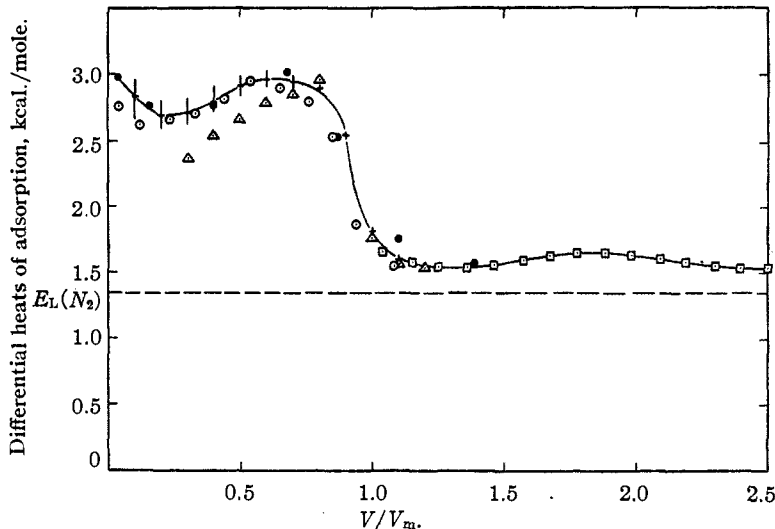


Fig. 6.—Differential heats of adsorption for nitrogen on Graphon as determined calorimetrically by Beebe, Biscoe, Smith and Wendell,<sup>2a</sup> (O, ●), and isothermally by the authors (+, -194.8 to -182.8°; Δ, -204.7 to -182.8°; □, -204.7 to -194.8°). The length of the vertical lines represents the total spread of the values calculated from the isothermic data.

discussed by Barrer<sup>11</sup> may cause a more orderly adsorption of the remainder of the monolayer, hence giving rise to the negative entropy change. It must be admitted, however, that it stretches

(11) Barrer, *Proc. Roy. Soc. (London)*, **161A**, 476 (1937).

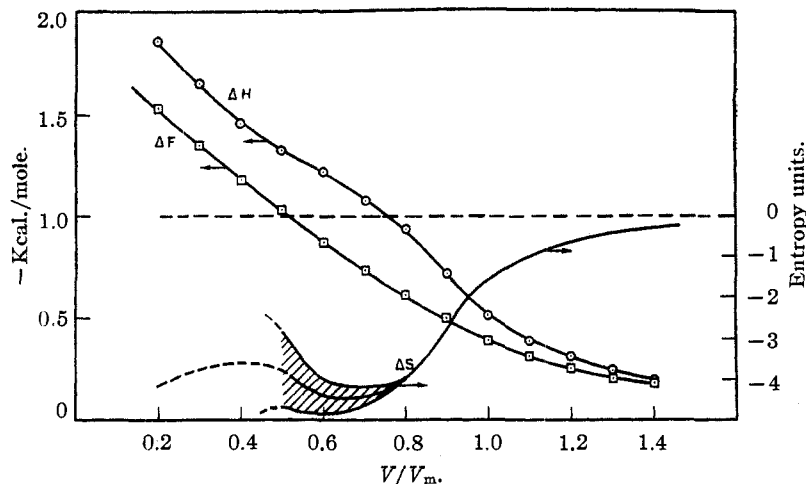


Fig. 7.—Variation in free energy change, change in heat content and entropy change for the transfer of nitrogen from the liquid state to the adsorbed state on Grade 6 Spheron with the system at  $-194.6^{\circ}$ .

this picture rather far to imagine this process being repeated to explain the positive entropy which appears in the second layer.

**Surface Area Measurements on the Carbon Blacks.**—In Figure 9, the data for the adsorption of nitrogen on Graphon are plotted according to the usual B.E.T. linear equation. At all three temperatures excellent straight lines are obtained up to 0.2 relative pressure. Above this pressure the experimental points fall below the B.E.T. plot. This behavior has been noted twice before in the literature, once with butane on silica gel<sup>6</sup> and once with nitrogen on activated magnesia.<sup>12</sup> There has been little basis for judging the course of this behavior in the first two instances. The points could fall below the B.E.T. curves either because  $E_2$ , the heat of adsorption in the second layer was higher than  $E_L$ , or as suggested by Walker and Zettlemoyer<sup>13</sup> because of the presence of a considerable amount of surface characterized by a low  $C$  value (2 to 10) in addition to the surface having the usual  $C$  value (50 to 150). In the B.E.T. plots of the nitrogen adsorption on Graphon shown in Fig. 9, it seems reasonable to attribute the behavior to the same cause that is responsible for a rise in the heat of adsorption in the range between adsorption volumes equivalent to 0.5 and 0.9 fraction of a monolayer and 1.6 and 1.8 monolayers. It seems ex-

(12) Zettlemoyer and Walker, *Ind. Eng. Chem.*, **39**, 69 (1947).

(13) Walker and Zettlemoyer, *J. Phys. and Colloid Chem.*, **52**, 47 (1948).

remely unlikely that the explanation suggested by Walker and Zettlemoyer<sup>13</sup> can explain the results in Fig. 9 because on no carbon black so far studied has  $C$  ever been lower than about 100 and because such low  $C$  values as would be necessary have never been observed for nitrogen adsorption on any solid except hide.<sup>14</sup>

$V_m$  for Graphon was calculated by the usual B.E.T. method from the linear portion below 0.2 relative pressure. The cross-sectional area of the nitrogen molecule was calculated for the various temperatures from the equation given by Emmett and Brunauer<sup>15</sup> using the data of Yost and Russell,<sup>16</sup> for the density of  $V_m$  and the cross-sectional area  $F$  (in sq. m./cc.) are given in Table I.

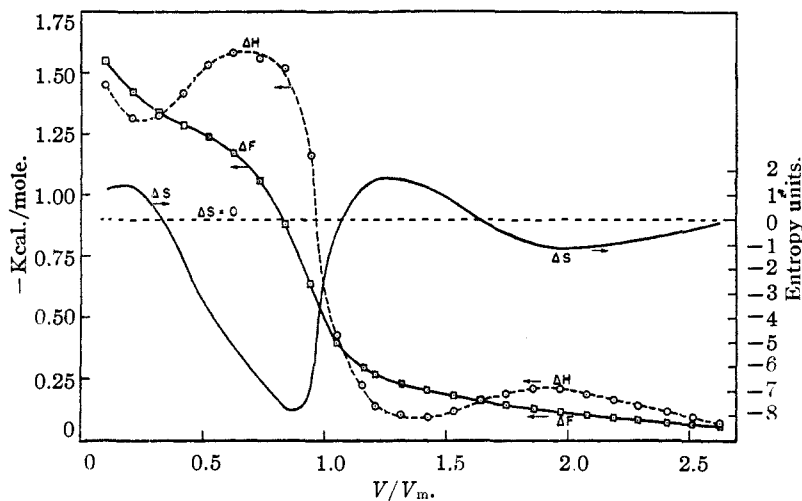


Fig. 8.—Variation in the free energy change, change in heat content and entropy change for the transfer of nitrogen from the liquid state to the adsorbed state on Graphon with the system at  $-194.8^{\circ}$ .

TABLE I

$V_m$ , surface area and  $C$  values for Graphon and for Grade 6 Spheron at various temperatures as determined from the B.E.T.<sup>5</sup> plot of the nitrogen adsorption isotherms.

	Temp., °C.	$V_m$ , cc./g.	Vol. factor $F$ , sq. m./cc.	Area, sq. m./g.	$C$
Graphon	-182.8	17.48	4.605	80.50	285
	-194.8	18.28	4.394	80.32	273
	-204.7	18.97	4.240	80.43	263
Spheron	-183.1	26.23	4.601	120.7	100
	-194.6	27.41	4.398	120.5	166

(14) Zettlemoyer, Schweitzer and Walker, *J. Am. Leather Chemists' Assoc.*, **41**, 253 (1946).

(15) Emmett and Brunauer, *THIS JOURNAL*, **59**, 1553 (1937).

(16) Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall Inc., New York, N. Y., 1944, p. 5.

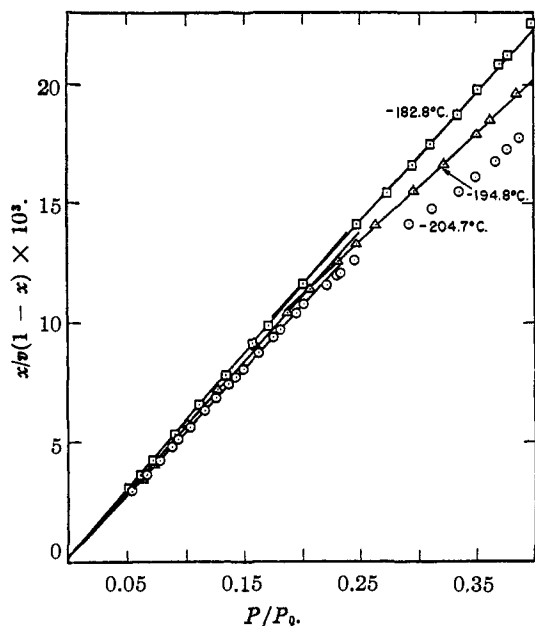


Fig. 9.—B. E. T.<sup>8</sup> plots of the three isotherms of nitrogen on Graphon.

The areas calculated by multiplying these two agree for all three temperatures within one per cent. This is an excellent confirmation of the variation with temperature of the cross-sectional area of the adsorbed nitrogen molecule as calculated by the equation of Emmett and Brunauer.<sup>15</sup> It also justifies the selection of the lower linear portion of Fig. 9 for the determination of  $V_m$  since no such agreement occurs if the upper, apparently linear, portion is used.

This break in the B.E.T. plot for the Graphon data accounts for the discrepancy between the value of  $V_m$  of Beebe, Biscoe, Smith and Wendell<sup>2a</sup> and that reported here. In determining  $V_m$  they used an average straight line and hence their value of 19.17 cc. is 5.5% above that obtained from the lower linear portion of the  $-194.8^\circ$  curve in Fig. 9. In Fig. 6, Beebe's value of  $V_m$  was used to calculate the fraction of the surface covered in order to keep both heat values on the same basis.

Figure 10 shows the Graphon data plotted according to the method of Harkins and Jura.<sup>4</sup> Again two linear portions occur with the break occurring at 0.2 relative pressure. This pressure is almost exactly where the hump in the isotherm begins. Indicated in Fig. 10 is the slope which the  $-194.8^\circ$  line should have if it is to give the same area by the Harkins and Jura<sup>4</sup> method as was obtained by the B.E.T. method. The slope of the linear portion occurring at low pressure is closer to this slope than

that of the higher pressure data. A  $\pi$ - $\sigma$  plot of the Graphon data showed no evidence of a phase change occurring in this system.

Both the B.E.T. and the Harkins and Jura plot of the Spheron isotherms are quite normal.

Table II gives the area of the two carbon blacks as determined by the B.E.T. method at the various temperatures and also the area obtained from the  $-194.8^\circ$  isotherm by the Harkins and Jura<sup>4</sup> method using 4.06 for the proportionality constant  $k$ . Isotherms at temperatures other than  $-194.8^\circ$  could not be used for Harkins and Jura determinations since  $k$  is not known for nitrogen except at that temperature. The B.E.T. results for both blacks are surprisingly self-consistent, the maximum variation among the areas for a given adsorbent being less than 1%. The agreement between the B.E.T. values and the Harkins and Jura value is also remarkably good, being within about 10%. As a matter of fact, it is interesting to note that the cross-sectional areas that have to be assigned to the nitrogen molecule to obtain surface areas by the B.E.T. method in agreement with those obtained by Harkins and Jura plots exhibit the same relationship to the constant  $C$  shown by one of the authors<sup>8</sup> to exist for numerous adsorptions being 17.93  $\text{\AA}^2$  and 17.04  $\text{\AA}^2$  for  $C$  values of 273 and 166, respectively.

Utilizing the slope of the Harkins and Jura plot of the isotherms at temperatures other than  $-194.8^\circ$  and the area, calculated from the  $-194.8^\circ$  data by their method, it is possible to

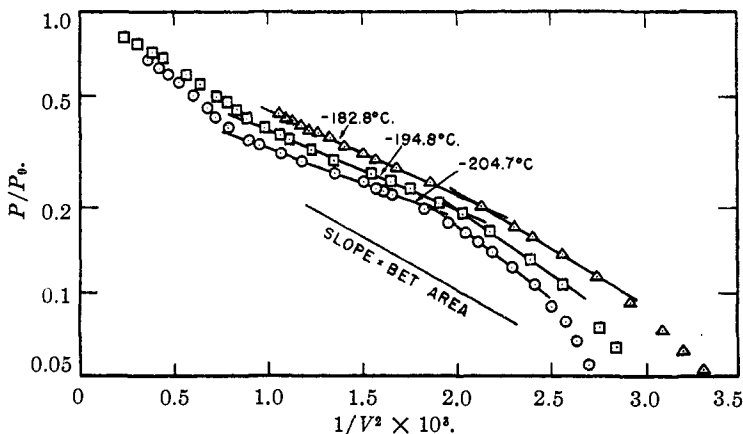


Fig. 10.—Harkins and Jura<sup>4</sup> plots of the three isotherms of nitrogen on Graphon. For comparison is shown the slope required to equal the B. E. T.<sup>8</sup> area for the  $-194.8^\circ$  isotherm.

calculate a value of the Harkins and Jura<sup>4</sup> proportionality constant  $k$  at the other temperatures. The results of such calculations are shown in the last two columns of Table II. The agreement between calculated  $k$  values for the two non-porous carbon blacks at  $-182.8^\circ$  is remarkable and is an excellent confirmation of the self-consistency of the Harkins and Jura<sup>4</sup> method when applied to non-porous substances. Incidentally, the varia-

tion of  $k$  with temperature in Table II is in approximate agreement with the prediction of Davis and DeWitt<sup>17</sup> that the Harkins and Jura  $k$  value for a given adsorbate should be proportional to  $1/T^{1/2}$ .

TABLE II

Comparison of areas of Graphon and Grade 6 Spheron as determined by the B. E. T. method<sup>6</sup> at three temperatures and by the Harkins and Jura method<sup>4</sup> at  $-195^\circ$ .

Temp., °C.	Area, sq. m./g.— B. E. T.			H & J $k =$ 4.06 area at $-195^\circ\text{C.}$	$k$ calculated from H & J	
	-195	-183	-205		-195	-183
Graphon	80.3	80.5	80.4	88.7	4.47	3.86
Spheron	120.4	120.7		126.3	4.47	

### Summary

1. Adsorption isotherms for nitrogen on two

(17) Davis and DeWitt, *THIS JOURNAL*, **70**, 1135 (1948).

samples of carbon black were determined at  $-205$ ,  $-195$  and  $-183^\circ$ .

2. The differential heats of adsorption of nitrogen on the two samples of carbon black were measured isothermally.

3. Excellent agreement with the calorimetric data of Beebe and his co-workers<sup>2a</sup> for the same samples of carbon black was obtained.  $\Delta F$  and  $\Delta S$  values for the process liquid nitrogen going to adsorbed nitrogen were determined as a function of the surface covered and a possible interpretation of the results is suggested.

4. The areas of the various samples as calculated by the B.E.T.<sup>5</sup> theory were compared to the areas calculated by the method of Harkins and Jura.<sup>4</sup>

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## Differential Heats of Adsorption and Desorption of Nitrogen on Porous Glass

BY L. G. JOYNER AND P. H. EMMETT

Gleysteen and Deitz<sup>1</sup> recently calculated by the Clausius-Clapeyron equation from the data of Lambert and Clark<sup>2</sup> the differential heat of adsorption and the differential heat of desorption of benzene on ferric oxide gel. They found the heat of desorption to be about 760 calories larger in the region where hysteresis occurs and suggested that this value could be used in conjunction with the Brunauer, Deming, Deming and Teller<sup>3</sup> adsorption equation to account approximately for the hysteresis observed in this benzene-iron oxide gel system.

It was felt that these observations of Gleysteen and Deitz<sup>1</sup> were of sufficient importance to warrant their being checked by another set of data. To this end we have determined the adsorption and desorption isotherms for nitrogen at  $-204.8^\circ$  and  $-194.6^\circ$  on a sample of porous glass.

### Experimental

**Materials.**—The porous glass sample was one of a number furnished by the Corning Glass Company (Hood and Nordberg, U. S. Patent 2,106,774). It was one of the samples used by Emmett and Cines<sup>4</sup> for adsorption work at  $-195^\circ$ .

The nitrogen adsorbate was Airco prepurified nitrogen. It was merely dried in a liquid nitrogen trap prior to being used.

**Apparatus.**—The adsorption and temperature controlling apparatus and the procedure were the same as for the preceding paper.<sup>5</sup> All surface area values were calculated by the standard B. E. T. equation.<sup>6</sup>

(1) Gleysteen and Deitz, *J. Research Nat. Bur. Standards*, **35**, 285 (1945).

(2) Lambert and Clark, *Proc. Roy. Soc.*, **A122**, 497 (1929).

(3) Brunauer, Deming, Deming and Teller, *THIS JOURNAL*, **62**, 1723 (1940).

(4) Emmett and Cines, *J. Phys. & Colloid Chem.*, **51**, 1248 (1947).

(5) Joyner and Emmett, *THIS JOURNAL*, **70**, 2353 (1948).

(6) P. H. Emmett, "American Society for Testing Materials, Symposium on New Methods for Particle Size Determination," 1941, p. 95.

### Results

The adsorption and desorption data for nitrogen on the porous glass have been plotted in Fig. 1. For each temperature, adsorption and desorption points for two separate runs are shown. The agreement between the separate runs was excellent. The isotherms are what have been called "Type IV" and resemble somewhat the isotherms obtained by Lambert and Clark<sup>2</sup> for benzene on iron oxide gel.

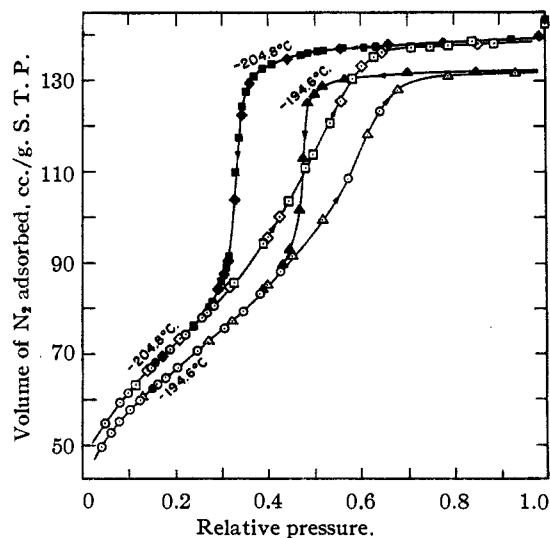


Fig. 1.—Adsorption of nitrogen on porous glass at  $-204.8$  and  $-194.6^\circ$ . Solid symbols are desorption points.

### Calculations and Discussion

**Comparison of the Heat of Adsorption of Nitrogen with the Heat of Desorption.**—Brunauer, Deming, Deming and Teller<sup>3</sup> de-