

tion of k with temperature in Table II is in approximate agreement with the prediction of Davis and DeWitt¹⁷ 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. method⁶ at three temperatures and by the Harkins and Jura method⁴ at -195° .

Temp., °C.	Area, sq. m./g.— B. E. T.			H & J $k =$ 4.06	k calculated from H & J area at -195°C.	
	-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° .

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^{2a} for the same samples of carbon black was obtained. ΔF and ΔS 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.⁵ theory were compared to the areas calculated by the method of Harkins and Jura.⁴

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Differential Heats of Adsorption and Desorption of Nitrogen on Porous Glass

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Gleysteen and Deitz¹ recently calculated by the Clausius-Clapeyron equation from the data of Lambert and Clark² 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 Teller³ 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 Deitz¹ 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° and -194.6° 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 Cines⁴ for adsorption work at -195° .

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.⁵ All surface area values were calculated by the standard B. E. T. equation.⁶

(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 Clark² for benzene on iron oxide gel.

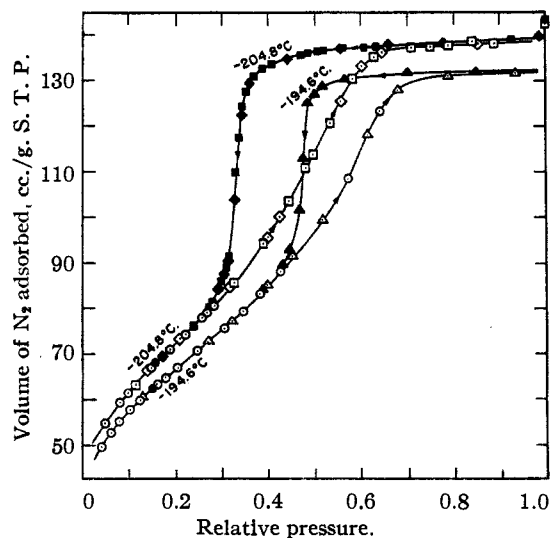


Fig. 1.—Adsorption of nitrogen on porous glass at -204.8 and -194.6° . Solid symbols are desorption points.

Calculations and Discussion

Comparison of the Heat of Adsorption of Nitrogen with the Heat of Desorption.—Brunauer, Deming, Deming and Teller³ de-

veloped a general adsorption theory by which five types of adsorption isotherms may be deduced from the single equation

$$V = V_m \left[\frac{x}{1-x} + A \right] \quad (1)$$

where A is a complicated function of C , x , \bar{n} and h . V_m is the volume of gas required to form a monolayer on the surface and x is the relative pressure. In the function A of equation 1, \bar{n} is the maximum number of layers that can fit into a capillary; C is related to the heat of adsorption of the first layer in the same way as in the regular B.E.T. equation⁶; and $h = (\bar{n}C^2 - C^2 + 2C) \exp. Q/RT$ where Q is an additional energy term associated with the last layer to enter the capillary.

Brunauer, Deming, Deming and Teller³ applied the above equation to the data of Lambert and Clark² for the adsorption of benzene on ferric oxide gel and obtained reasonably good agreement. Gleysteen and Deitz¹ showed that if all the constants of Equation 1, as calculated from the adsorption data, are held fixed except for the value of Q and, if this is increased by the 760 calories that they had calculated as the amount by which the heat of desorption of benzene on ferric oxide gel exceeded the heat of adsorption, a reasonable facsimile of the experimental desorption curve is obtained.

In applying the suggestion of Gleysteen and Deitz¹ to our data we have elected to assign such excess heat to the Q for desorption as is needed to make the desorption isotherm for -194.6° as calculated from equation 1 agree with that shown in Fig. 1. The curve for this calculated excess Q (labeled calcd. B.D.D.T.) is shown in Fig. 2. It is apparent that no single value for the amount by which the Q for the desorption curve exceeds that for the adsorption curve would suffice to give agreement between the experimental and calcu-

lated isotherms. Furthermore, it is evident that at low relative pressures and at high relative pressures the heats of adsorption and desorption will be equal.

Some explanation of how the calculated curve (marked B.D.D.T. calcd. in Fig. 2) for the heat of desorption minus the heat of adsorption was obtained may be in order. The values for V_m and C for the -194.6° isotherm were obtained in the usual manner from the simple B.E.T. plot (see equation 1 of the preceding⁵ paper). The values of the parameters \bar{n} and Q which gave the best fit of Equation 1 to the adsorption isotherm were then determined by a trial and error method. The Q so determined may be designated as Q_{ads} . Agreement between experiment and theory was obtained to about the same degree as was obtained by Brunauer, Deming, Deming and Teller³ for the benzene-ferric oxide system. Using the values of V_m , C and \bar{n} from the adsorption part of the curve, values of V and x from the desorption isotherm were inserted into Equation 1 and Q_{des} calculated. The calculated curve of Fig. 2 is simply $Q_{\text{des}} - Q_{\text{ads}}$ plotted as a function of the relative pressure at -194.6° .

The conventional isosteric calculation of heats of adsorption and desorption by the Clausius-Clapeyron equation is fraught with considerable uncertainty when applied to data such as shown in Fig. 1. As pointed out by McBain⁷ it is impossible to construct isosteres for the higher relative pressure regions for those cases in which the volume of gas adsorbed (S.T.P.) at saturation varies with temperature. The difficulty can apparently be avoided if one applies the Clausius-Clapeyron equation at constant liquid volume (and hence constant volume of pore space filled with adsorbate) rather than to constant volume of gas adsorbed. The amount by which the heat of desorption exceeds the heat of adsorption per mole is shown in Fig. 2 as a function of the relative pressure (for the -194.6° isotherm) when calculated both on the basis of constant liquid volume of adsorbate and also when calculated for constant number of moles of adsorbate on the porous glass.

From what has already been said, it follows that curve 3 cannot be extended above about 0.7 relative pressure because at this point the isotherm for -194.6° levels off and becomes independent of pressure.

The three curves shown in Fig. 2 are in remarkably good agreement considering the assumptions involved in the Brunauer, Deming, Deming and Teller³ theory and the methods used in calculating curve 2. They all combine to indicate that the quantity of heat involved in desorbing adsorbate from capillaries is greater than the heat evolved during adsorption. This excess heat is probably of fundamental importance in determining the cause of the hysteresis loop, though the exact relationships involved may remain obscure until

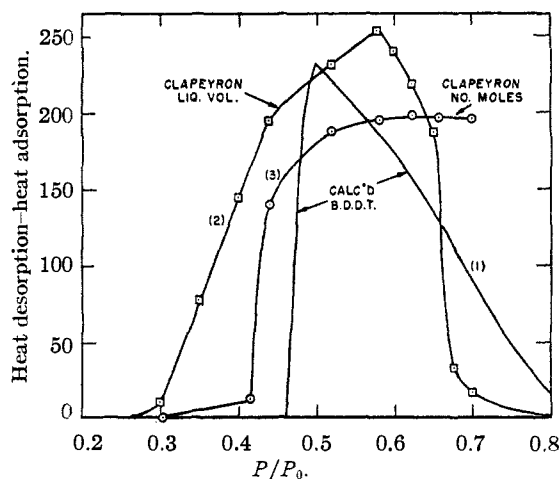


Fig. 2.—Excess of the heat of desorption over the heat of adsorption for nitrogen (in calories per mole) on porous glass over the hysteresis region, as calculated by three different methods

(7) McBain, "The Sorption of Gases and Vapors by Solids," G. Routledge and Sons Ltd., London, 1932, p. 141.

more is learned concerning the phenomenon of hysteresis.

Variation of the Inception of Desorption Hysteresis with Temperature.—One other observation relative to the isotherms in Fig. 1 is of interest. A few years ago, Cohan,⁸ on the basis of an "open pore" theory of adsorption, predicted that the lower relative pressure at which the desorption branch of an isotherm rejoins the adsorption branch should decrease as the temperature decreases. Qualitatively our data shown by the plots in Fig. 1 and similar data by Lambert and Clark² for benzene adsorption on ferric oxide agree with Cohan's hypothesis.⁸ However, the agreement with his prediction is not quantitative. Thus, the value of the relative pressure corresponding to the beginning of hysteresis at -204.8° should be 0.305 according to Cohan⁸ if, as in Fig. 1, the corresponding relative pressure in the -194.6° isotherm is 0.420. Actually, the hysteresis at -204.8° begins at about 0.265 relative pressure.

Surface Area Measurements on Porous Glass.—The adsorption data at both temperatures yield excellent linear portions when plotted according to either the B.E.T.⁶ or the Harkins and Jura⁹ method. The B.E.T. areas and C values for porous glass as calculated from both the -194.6° and the -204.8° isotherms are given in Table I. The Harkins and Jura area was calculated from the -194.6° isotherm by the use of 4.06 for the proportionality constant k . The agreement between the B.E.T. areas, although not as good as for the carbon blacks of the preceding paper, is still within 2%. Again the Harkins and Jura area is somewhat higher than but nevertheless is in reasonable agreement with that obtained by the

TABLE I

Calculation of the surface areas and related constants by the B. E. T.⁶ and by the Harkins and Jura⁹ methods from the nitrogen adsorption isotherms:

Temperature, °C.	-194.6	-204.8
V_m , cc./g.	55.90	59.21
B.E.T. area, sq. m./g.	245.8 ^a	250.9 ^a
H. & J. area, sq. m./g.	255.2	
k calculated from H. & J. area at -194.6°C .		3.35
B.E.T. C	123	147

^a The cross-sectional molecular areas for nitrogen for -194.6° and -204.8° were taken as 16.26\AA^2 and 15.67\AA^2 , respectively, for these area calculations.

(8) Cohan, *THIS JOURNAL*, **66**, 98 (1944).

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

B.E.T. method. We find as in the preceding paper⁶ that the cross-sectional area (16.9\AA^2) that has to be assigned to the nitrogen molecule to obtain a surface area by the B.E.T. method in agreement with that obtained by the Harkins and Jura⁹ plot exhibits the same relationship to the constant C (123) which has been shown to exist by one of the authors.¹⁰

If we utilize the slope of the Harkins and Jura⁹ plot for the -204.8° isotherm and calculate a value of the Harkins and Jura proportionality constant k required to yield the same value of the surface area as was obtained by their method from the data at -194.6° , we obtain a value for k of 3.35 for the porous glass. A similar calculation in the preceding paper⁶ for the non-porous solid Graphon at the same temperature yielded a k value of 3.86. This difference of about 17% in the value of k found between the porous and non-porous substances at -204.8° is to be compared to the perfect agreement between k values found for the two non-porous carbon blacks at -183° in the preceding paper.⁶ These two examples are insufficient to warrant final conclusions but they do suggest that the temperature coefficient of k may be different for porous and non-porous substances.

Summary

1. Adsorption isotherms for nitrogen on a sample of porous glass were determined at -204.8° and -194.6° .

2. The differential heat of adsorption and the differential heat of desorption of nitrogen on the porous glass were measured isothermally.

3. For the porous glass the differential heat of desorption was shown to be in excess of the differential heat of adsorption over the hysteresis region by as much as 250 calories. The excess heat of desorption over the heat of adsorption was correlated with the hysteresis loop by means of the Brunauer, Deming, Deming and Teller³ theory of multilayer adsorption in a way similar to that suggested by Gleysteen and Deitz.¹

4. The area of the porous glass as calculated by the B.E.T.⁶ theory from the adsorption data at -194.6° was compared to and found to agree with the area calculated by the method of Harkins and Jura.⁹

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