experiments continued for an hour, and, in a test case, for many hours. If the criticism were here valid, the liquid must be supposed to occupy perhaps ten minutes in developing about 95% of its equilibrium vapor pressure and thereupon to reach a state stationary for hours.

d. The possibility of superheating cannot come in question with our method of work.

e. The likelihood of phosphorus pentoxide reacting with benzene to produce a soluble impurity of lower volatility than benzene[29] is negatived by the results of expts. 1, 9, 10, 11, 12 and 18 which, over many weeks, showed no elevation of boiling point; of expts. 2, 13 and 15 whose boiling points reverted to normal upon heating; and of expts. 5 and 8 which reverted to normal b. p. upon opening to the atmosphere.

Summary

When purified benzene was desiccated with purified phosphorus pentoxide with precautions to exclude or destroy dust, its vapor pressure, near 80°, was (a) lowered markedly if the drying process had been carried on at room temperature, and (b) raised slightly if the drying process had been carried on at 90 or 105°. Without opening the sealed apparatus, the vapor pressure could be caused to revert to the normal value by heating the liquid in the apparatus out of contact with the desiccant, provided that the desiccation had not been too rigorous. Upon allowing access of ordinary air, vapor pressures likewise reverted to normal value.

No change was found under like conditions in the vapor pressure of benzene if the materials used were not both purified and also dust free, nor when barium oxide or magnesium perchlorate were used as desiccants.

Carbon tetrachloride, normal heptane and cyclohexane all failed to show any change in vapor pressure upon desiccation under the same conditions that had given positive results in the case of benzene.

PRINCETON, N. J. RECEIVED SEPTEMBER 22, 1937

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[29] *Cf.* D. Balareff, *J. prakt. Chem.*, **116**, 57 (1927).

[CONTRIBUTION FROM THE U. S. DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY AND SOILS]

The Use of Low Temperature van der Waals Adsorption Isotherms in Determining the Surface Areas of Various Adsorbents

BY STEPHEN BRUNAUER AND PAUL H. EMMETT

In a number of previous publications[1-3] we proposed a method by which one can evaluate the surface area of iron synthetic ammonia catalysts from adsorption isotherms determined at or near the boiling points of the gases adsorbed. In the present paper we are reporting the results obtained in applying the method to other catalysts, catalyst supports, and various finely divided materials.

Experimental

The apparatus, experimental procedure and the nature of the constant temperature baths have all been described previously.[2,3,4] The "dead space" around the adsorbents was measured with helium. The measured gas volumes were all corrected for the deviations from the perfect gas laws, the percentage deviations used being the same as in a previous paper.[3]

Included in the present work are isotherms for the adsorption of argon and nitrogen at −195.8°; nitrogen, argon, carbon monoxide, and oxygen at −183°; carbon dioxide at −78°; normal butane and sulfur dioxide at 0°. The preparation and purification of all of these gases except sulfur dioxide have been described already.[2,3] Tank sulfur dioxide from the Baker Chemical Company was dried over Dehydrite and used without further purification after it had been shown to contain less than 0.02% inert gases and no sulfur trioxide.

The eighteen adsorbents used in the work described in the present paper are numbers 13 to 30 inclusive in Table III. Similar experiments on soils and soil colloids have been reported in another paper.[5]

One of the two copper catalysts was prepared by Mr. J. F. Shultz of this Laboratory by melting electrolytic copper in an oxy-hydrogen flame in the presence of excess oxygen, crushing the resulting copper oxide to approximate mesh size, and reducing it in hydrogen at 200°. The other copper catalyst was obtained by reducing a commercial copper oxide (Eimer and Amend C. P. cupric oxide) at 200°. Each reduction was started at 200° but was so exothermic as to proceed rapidly after the removal of the furnace. Before each adsorption run the copper catalysts were reduced in hydrogen for one hour at 300° and then evacuated for an hour at the same temperature.

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[1] Brunauer and Emmett, THIS JOURNAL, **57**, 1754 (1935).

[2] Emmett and Brunauer, *ibid.*, **59**, 310 (1937).

[3] Emmett and Brunauer, *ibid.*, **59**, 1553 (1937).

[4] Emmett and Brunauer, *ibid.*, **56**, 35 (1934).

[5] Emmett, Brunauer and Love, *Soil Science* (to be published).

Glaucosil is the trade name[6] applied to the insoluble residue that remains after the extraction of green sand by sulfuric acid. It is a non-crystalline highly porous form of silica which when washed and dried is a very satisfactory adsorbent. The samples were evacuated at 100° for two hours before each adsorption run.

Commercial pumice was purified by boiling in 15% nitric acid for half an hour. It was washed twenty times in distilled water and dried at 120° for several days. Finally it was dried in a stream of nitrogen at 350° for seven hours. Before each run the sample was evacuated at 350° for one hour. Another pumice sample, purified in the same manner, was soaked in a nickel nitrate solution containing 0.0789 g. of nickel per cc., dried in an oven at 120°, and then gently ignited until nitrogen dioxide fumes ceased to be evolved. Finally a stream of dry air was passed over the catalyst at 350° for seven hours. Before each run the sample was evacuated for an hour at 350°. The supported nickel catalyst was prepared by reducing the above supported nickel oxide catalyst for four hours at 350° in hydrogen. An additional hour's reduction and an hour's evacuation was carried out before each run.

Dried azotobacter cells were prepared by Dr. H. Lineweaver, as already described.[7] Runs were made both before and after powdering the samples in a steel ball mill. Prior to the adsorption runs evacuation was carried out at room temperature for one hour.

Chromic oxide gel was prepared by the method used by Howard and Taylor.[8] It was dried in an oven up to 190° and finally dried *in situ* in a stream of nitrogen for four hours. Evacuation for an hour at 350° preceded each run. On heating the sample at 350° in hydrogen the characteristic "glowing" occurred. The glowed sample was heated in hydrogen for an hour and evacuated a similar time at 350° before each run.

A sample of potassium chloride was obtained by grinding the standard Mallinckrodt analytical reagent grade (99.96% pure) potassium chloride in a ball mill and using the portion that passed through a 200-mesh sieve. The sample was evacuated at 200° for an hour before each run.

Copper sulfate pentahydrate of Mallinckrodt analytical reagent grade (99.87% pure) was crushed and screened to 40–100 mesh size. It was evacuated for one hour at room temperature before being used. The anhydrous copper sulfate was obtained by heating this same sample of pentahydrate in a stream of air at temperatures increasing gradually to 350° and then evacuated for forty-eight hours at 350°.

Two samples of silica gel have been used; they were kindly furnished to us by Drs. L. H. Reyerson and R. E. Clark of the Minnesota Institute of Technology. They inform us that "the samples were prepared by the method of Patrick,[9] purified by hot concentrated nitric acid, washed repeatedly by conductivity water, and dried in air at 100°. One of the samples (Sample II) was electrodialyzed until it was ion free."

Activated charcoal from the Fisher Scientific Company was first evacuated at 500° for three days and then for an additional seventeen hours before each run. Two samples of activated carbon obtained from the Darco Corporation and designated as Darco B and Darco G were treated in the same way as charcoal before being used.

Results

The experimental results are shown in Figs. 1 to 8. The gases to be adsorbed were so chosen that the low temperature adsorption would not be complicated by chemisorptions of the type described in previous papers.[1–3]

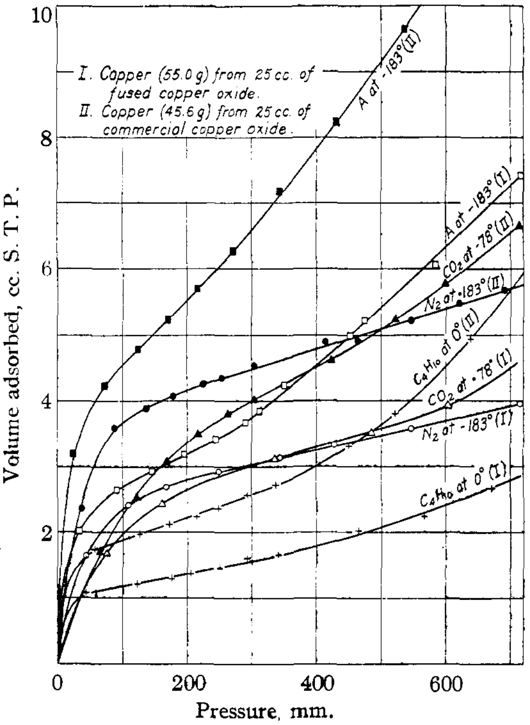

Fig. 1.—Low temperature adsorption isotherms on two copper catalysts.

The isotherms are for the most part self-explanatory though a few additional remarks in regard to them seem desirable.

Heating the pumice sample (Fig. 2) to 500° in hydrogen for seven hours produced no change in surface. However, the nickel catalyst supported on pumice suffered a 50% decrease in surface on being heated for seven hours in hydrogen at 520°.

Adsorption isotherms for the bacteria samples are not shown because they have been published elsewhere.[7] It will suffice to point out that a 17.5-g. sample of the dry powdered bacteria gave a typical nitrogen isotherm at −183°, the adsorption being 13 cc. at 400 mm. The adsorption on this sample before pulverization was only 0.65 cc. at the same pressure.

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[6] Turrentine, "Potash," John Wiley and Sons, New York, pp. 109-112.

[7] Lineweaver, *J. Biol. Chem.* (to be published).

[8] Howard and Taylor, THIS JOURNAL, **56**, 2259 (1934).

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

In Fig. 3 the right-hand ordinate refers to the adsorption on the chromic oxide gel, the left-hand ordinate to the adsorption after the gel had been "glowed." There was more than a sevenfold decrease in adsorption due to "glowing." The weight given in the figure was obtained when the sample of chromium oxide gel had been dried up to 190°.

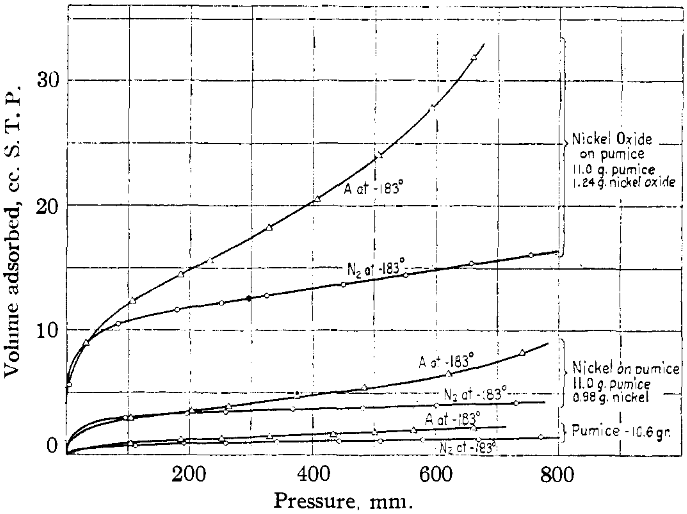

Fig. 2.—Low temperature adsorption isotherms on pumice, nickel oxide supported on pumice and nickel supported on pumice. (25 cc. samples were used in each instance.)

In Fig. 4 the left-hand ordinate refers to the adsorption of argon on potassium chloride and $CuSO_4 \cdot 5H_2O$, the right-hand one to the adsorption on the dehydrated $CuSO_4$. Dehydration apparently increased the adsorption per mole of $CuSO_4$ about twenty-threefold (at 400 mm). Desorption points (solid triangle and circle) were taken on the runs represented by curves 1 and 3, Fig. 4, to be sure that complete equilibration was being obtained.

Evacuating the glaucosil sample (Fig. 5) for twenty hours at 500° did not alter its adsorption capacity for either nitrogen or butane.

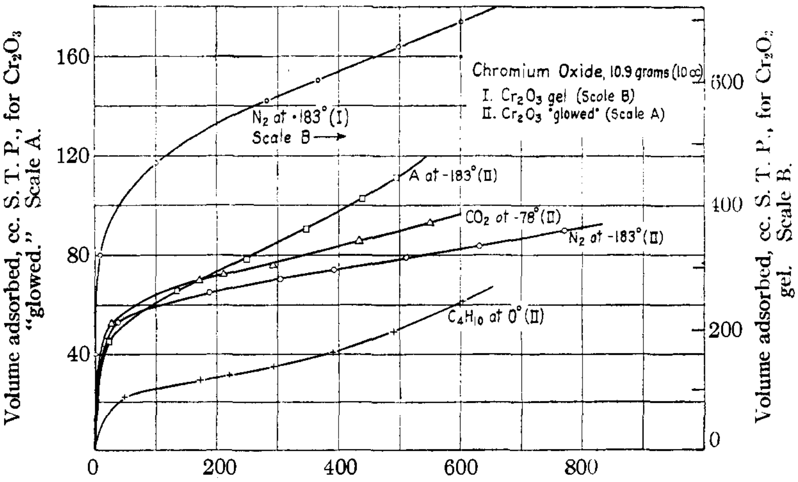

Fig. 3.—Low temperature adsorption isotherms on chromium oxide gel, and on "glowed" chromium oxide.

One nitrogen and one oxygen run at −183° were performed on the electrodialyzed silica gel. These runs were very similar to the corresponding ones on the other sample (Fig. 6), the adsorption per unit weight being about 5% larger than for the non-electrodialyzed sample.

In evacuating the activated charcoal and carbon samples (Figs. 7 and 8) at only 500° we realized that we were probably not removing all the chemisorbed gases. However, since it was not convenient to use a higher temperature of evacuation and since the adsorption runs appeared to be entirely reproducible in spite of the low temperature of evacuation, the various isotherms that have been determined on these substances are included in the present paper. Flushing the charcoal sample with 500 cc. of hydrogen per minute at 500° for twenty-four hours did not change its sorptive capacity for oxygen at −183°.

Discussion

The isotherms obtained on all of the adsorbents except charcoal are S-shaped. It will be convenient, therefore, to discuss them separately from the results on charcoal.

The S-shaped isotherm consists of a low pressure portion concave to the pressure axis and a high pressure portion convex to the pressure axis. These curved extremities are connected by a well-defined linear portion whose length varies from one adsorbent to another. In a previous paper evidence relative to the physical and chemical adsorption of gases on iron synthetic ammonia catalysts has been presented to show that the be-

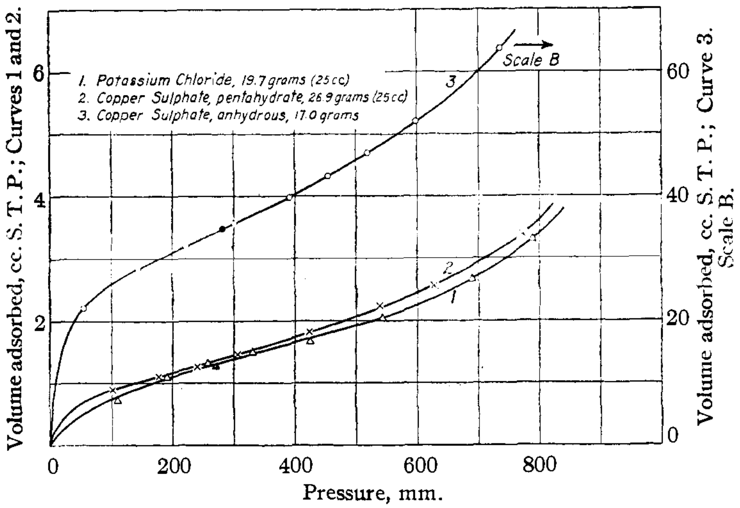

Fig. 4.—Adsorption isotherms of argon at −183° on potassium chloride, copper sulfate pentahydrate and anhydrous copper sulfate.

ginning of the linear portion of the low temperature isotherms (designated as point B) represents the point corresponding to the completion of a unimolecular layer. In the present paper we shall assume that the adsorption isotherms on the other adsorbents are to be interpreted in a similar manner and shall then proceed to see how good the agreement is among the surface area values calculated for a given adsorbent from isotherms for different gases.

In Table I the adsorption volumes corresponding to the beginning of the straight line portion of the isotherms (point B) are given for eight different adsorbents. The next two columns give the surface areas of the adsorbents calculated from the corresponding point B value by multiplying the number of molecules in the unimolecular layer by the area occupied by one molecule on the surface, the diameter of the molecule being calculated from the density of the liquefied (area (*L*)) and of the solidified (area (*S*)) gas, respectively. More details about this type of calculation together with a table of values of area (*L*) and area (*S*) for different molecules have been given in a previous article.[3] The following values that are not mentioned in that table are used in the present paper: argon at −195.8°, area (*S*), 12.8 sq. Å. and area (*L*), 13.8 sq. Å.; sulfur dioxide at 0°, area (*L*), 19.2 sq. Å. These values were obtained with the help of density data from the "International Critical Tables"; for the density of solid sulfur dioxide no data were available.

TABLE I

ADSORPTION VOLUMES AT POINT B AND EQUIVALENT AREAS ON VARIOUS ADSORBENTS

Adsorbent	Gas	Temp., °C.	Point B cc. S. T. P.	Area (*S*) sq. meter	Area (*L*) sq. meter
Cu (fused)	N_2	−183	2.8	10.5	12.9
55.0 g. (25 cc.)	A	−183	2.7	9.3	10.5
	CO_2	− 78	2.8	10.7	12.9
	C_4H_{10}	0	1.1	9.5	9.5
Cu (commercial)	N_2	−183	4.2	15.7	19.3
45.6 g. (25 cc.)	A	−183	4.4	15.2	17.1
	CO_2	− 78	3.8	14.5	17.5
	C_4H_{10}	0	1.7	14.7	14.8
NiO on pumice	N_2	−183	11.4	42.5	52.4
11.0 g. pumice +	A	−183	12.8	44.3	49.9
1.24 g. NiO (25 cc.)	C_4H_{10}	0	5.0	43.3	43.4
Cr_2O_3 "glowed"	N_2	−183	67	250	308
10.9 g. (10 cc.)	A	−183	67	232	261
	CO_2	− 78	68	259	313
	C_4H_{10}	0	24	208	208
Darco B	N_2	−183	59	220	271
0.470 g. (2 cc.)	O_2	−183	73	239	278
	C_4H_{10}	0	22	190	191
Darco G	N_2	−183	164	612	754
0.355 g. (3 cc.)	O_2	−183	216	706	824
	C_4H_{10}	0	62	536	538
Glaucosil	N_2	−195.8	150	560	657
8.01 g. (10 cc.)	N_2	−183	144	538	662
	A	−183	146	506	569
	C_4H_{10}	0	22	190	191
Silica gel	N_2	−195.8	82	306	359
0.606 g. (1 cc.)	N_2	−183	77	287	354
	A	−183	74	256	296
	O_2	−183	80	262	305
	CO	−183	80	296	363
	CO_2	− 78	62	237	285
	SO_2	0	42	...	218
	C_4H_{10}	0	17	147	148

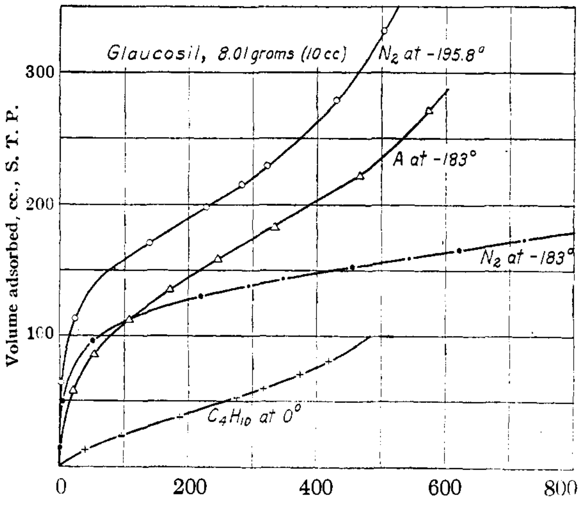

Fig. 5.—Low temperature adsorption isotherms on glaucosil.

An examination of Table I shows that the surface values obtained from the isotherms of the smaller molecules such as nitrogen, oxygen, argon, carbon monoxide and carbon dioxide for the different adsorbents are just as consistent as the surface area values obtained for the various iron synthetic ammonia catalysts. For the eight adsorbents the maximum deviations of any calculated surface area from the mean value obtained from all of the isotherms of the above gases obtained on the same adsorbent range from 2 to 13% when area (*S*) values are used and from 1 to 13% when area (*L*) values are used. Butane appears to give anomalous results. On some adsorbents the surface calculated from the butane isotherms is in very good agreement with the surface calculated from the other isotherms. Thus for the fused copper, commercial copper, and nickel on pumice the deviation from the mean is 7, 3 and 0%, respectively. For "glowed" chromic oxide, Darco G and Darco B the agreement is fair, the deviation from the mean being 16, 19 and 17% in these three instances. For silica gel and glaucosil, however, the butane isotherms for some as yet unknown reason give very poor agreement with the other isotherms, being 64% low for glaucosil and 46% for silica gel. It would appear, therefore, that to obtain the surface areas of adsorbents by selecting point B on the low temperature isotherms one preferably should use small molecules such as nitrogen, oxygen, argon, carbon monoxide or carbon dioxide. It may be added that the single run in which sulfur dioxide was used (on silica gel) gave a surface area which is intermediate between the surface obtained from butane and that obtained from the other gases, just as the sulfur dioxide molecule itself is intermediate in size between the butane molecule and any of the other molecules mentioned above.

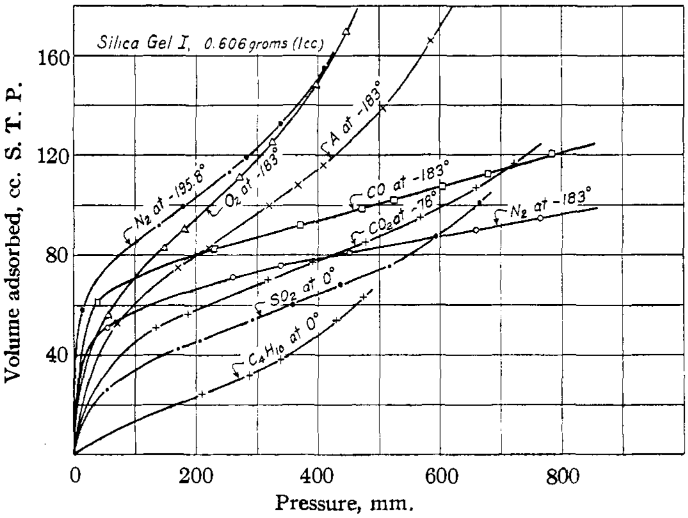

Fig. 6.—Low temperature adsorption isotherms on silica gel.

Some very interesting recent experiments of Palmer and Clark[10] relative to the adsorption of acetone, benzene and similar molecules on a measured surface of vitreous silica lead to conclusions that are in substantial agreement with our own. They measured the absolute surface area of powdered vitreous silica from measurements of the initial rate of solution of the powdered form in hydrofluoric acid compared to the rate of solution from a sample of known area. They also determined the adsorption isotherm of acetone on the same powder at 25°. The isotherm is S-shaped, with a rather long straight-line portion. If we take the beginning of this straight line portion as corresponding to one complete adsorbed layer, and multiply the number of acetone molecules adsorbed by the area occupied on the surface by an acetone molecule (area (*L*)), the area thus obtained is 8% larger

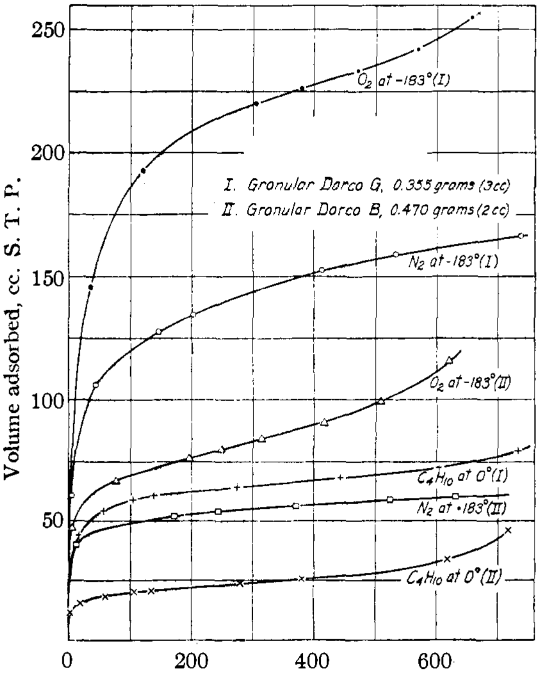

Fig. 7.—Low temperature adsorption isotherms on Darco B and Darco G.

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[10] Palmer and Clark, *Proc. Roy. Soc.* (London), **A149**, 360 (1935).

than that determined from the rate of solution in hydrofluoric acid. This remarkably close agreement between the two widely different methods of surface determination appears to be a striking confirmation of the reliability of both methods.

Since the isotherms that we obtained for the adsorption of various gases on charcoal (Fig. 8) are not S-shaped and have no linear portion, naturally the method of surface area measurement that seems applicable to all other adsorbents that we have tried cannot be used in this instance. However, the general shape of the isotherms on charcoal rather suggests that a unimolecular layer may be approached as p approaches the saturation pressure p_0. On this assumption the surface area of the charcoal sample that we used can be calculated. In Table II are listed the calculated values for the surface area both for area (L) and area (S) values per molecule. It will be noted that the area determined from one gas is closely the same as that determined from another except for butane. For charcoal as for several other adsorbents butane leads to surface area values that are too small. It seems probable that this may be caused by the inability of the butane molecules to penetrate into some of the capillaries to which the smaller molecules have access though this cannot be said with certainty at present.

TABLE II

ADSORPTION VOLUMES AT SATURATION PRESSURE ON CHARCOAL, AND EQUIVALENT AREAS

Weight of charcoal = 0.2 gram; volume = 0.5 cc.

Gas	Temp., °C.	Vol. ads., cc. S. T. P.	Area (S) sq. meter	Area (L) sq. meter
N_2	−195.8	35.4	132	155
N_2	−183	32.4[a]	121	149
A	−195.8	41.6	144	155
A	−183	41.4	143	161
O_2	−183	45.2	148	172
CO	−183	34.0[a]	126	154
CO_2	− 78	32.8[a]	125	151
C_4H_{10}	0	12.0	104	104

[a] Adsorption volumes around atmospheric pressure (not saturation pressure).

In Table III are compiled the surface areas in sq. meters per g. for the thirty adsorbents on which we have made measurements. The volume of gas required to form a unimolecular layer was taken as the volume at point B on the −183° nitrogen isotherms for all the adsorbents except KCl, $CuSO_4 \cdot 5H_2O$, $CuSO_4$ and charcoal. For the first three of these point B on the argon isotherms was used; for charcoal the value of nitrogen adsorption at −195.8° close to saturation pressure was considered a unimolecular layer. The molecular cross-sectional areas were calculated from the densities of the liquids.

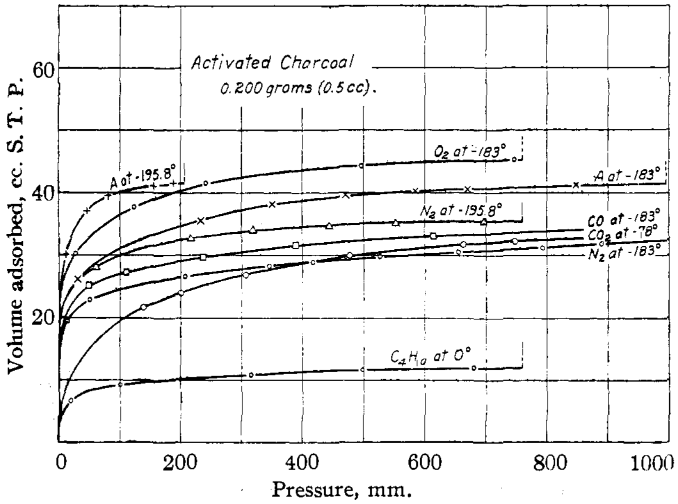

Fig. 8.—Low temperature adsorption isotherms on charcoal.

Several things of interest are to be noted in Table III. In the first place the remarkably large range of surface areas that one obtains among the various adsorbing materials is striking. For example, the specific surface of Darco G is 100,000 times that of unreduced Fe_3O_4 catalyst. At one end of the scale are the amorphous substances and gels; at the other the metals, metal oxides and salts. In this connection it is interesting to note that pumice, a commonly used catalyst support, actually has a comparatively small surface per unit weight. The nickel oxide supported on the pumice has a surface some eleven times that of the pumice itself.

A simple calculation will show that, at the points on the isotherms that we have designated as corresponding to unimolecular layers, one gas molecule is adsorbed for every three molecules of the adsorbent silica gel, for every six atoms of carbon in charcoal, and for every two atoms of carbon in Darco G (on the basis of the oxygen runs in Figs. 6, 7 and 8). Because of the difficulty of imagining a type of solid in which one out of every three or four of its atoms or molecules is on the surface some may be inclined to interpret the isotherms that we have obtained as due, in a large part, to capillary condensation. However, as we shall show in another paper, the same type of theory that explains the shape of the multi-

TABLE III

SPECIFIC SURFACE OF VARIOUS ADSORBENTS

	Adsorbent	Specific surface, sq. m./g.
1	Fe_3O_4 catalyst (unreduced)	0.02
2	Fe catalyst 973, sample I. Unpromoted, 0.15% Al_2O_3 impurity	0.55
3	Fe catalyst 973, sample II. Unpromoted, 0.15% Al_2O_3 impurity	1.24
4	Fe–Al_2O_3 catalyst 954. 10.2% Al_2O_3	11.03
5	Fe–Al_2O_3 catalyst 424. 1.03% Al_2O_3, 0.19% ZrO_2	9.44
6	Fe–Al_2O_3–K_2O catalyst 931. 1.3% Al_2O_3, 1.59% K_2O	4.78
7	Fe–Al_2O_3–K_2O catalyst 958. 0.35% Al_2O_3, 0.08% K_2O	2.50
8	Fe–K_2O catalyst 930. 1.07% K_2O	0.56
9	Cecil soil, 9418	32.3
10	Cecil soil, colloid, 9418	58.6
11	Barnes soil, 10,308	44.2
12	Barnes soil colloid, 10,308	101.2
13	Fused copper catalyst	0.23
14	Commercial copper catalyst	.42
15	Pumice	.38
16	Ni catalyst supported on pumice. 91.8% pumice	1.27
17	NiO catalyst supported on pumice. 89.8% pumice	4.28
18	Cr_2O_3 gel	228
19	Cr_2O_3 "glowed"	28.3
20	Glaucosil	82
21	Silica gel I (non-electrodialyzed)	584
22	Silica gel II (electrodialyzed)	614
23	Dried bacteria	0.17
24	Dried bacteria (pulverized)	3.41
25	KCl (finer than 200 mesh)	0.24
26	$CuSO_4 \cdot 5H_2O$ (40–100 mesh)	.16
27	$CuSO_4$, anhydrous	6.23
28	Granular Darco B	576
29	Granular Darco G	2123
30	Activated charcoal	775

molecular adsorption on iron catalysts appears to be applicable to all the S-shaped isotherms that we have obtained including those for the gels and other amorphous substances. We therefore are confident that at the relatively small p/p_0 values corresponding to point B the shapes of the isotherms in the present paper are not influenced by capillary condensation.

In conclusion attention should be called to the three argon adsorption isotherms given in Fig. 4. De Boer and Zwicker[11] and later Bradley[12] developed a theory according to which the building up of multimolecular adsorbed layers was attributed to successive polarization of each layer by the one below. Bradley concluded on the basis of this theory that no thick film of argon ought to build up on potassum chloride because of the small polarizing power of alkali metal ions and because of the approximate equality of the ionic radii of potassium and chlorine. On the other hand, such materials as anhydrous copper sulfate and aluminum sulfate would, he believed, yield 75 or more layers of multimolecular adsorption. In conformity with his theory, his adsorption measurements made on samples of potassium chloride and anhydrous copper sulfate having, presumably, approximately the same geometric surface area, as judged by measuring the average particle size with a microscope, showed no formation of multimolecular films of argon on potassium chloride at about 87°K., but typical S-shaped curves for this gas on anhydrous copper sulfate. In contradiction to his result and prediction curve 1 of Fig. 4 shows that a 200-mesh sample of potassium chloride gives the same typical S-shaped curve that is obtained on anhydrous copper sulfate and therefore apparently permits formation of multimolecular adsorption films on its surface. Furthermore, the dehydrating of copper sulfate pentahydrate resulted in a 39-fold increase in the specific adsorptive capacity (a 25-fold increase per mole of copper sulfate) as is evident from Table III, or curves 2 and 3, Fig. 4. These data, we believe, combine to establish the correctness of our previous suggestion[3] that the sample of dehydrated copper sulfate used by Bradley was so porous that its "inner surface" was of the order of 20 times as great as the microscopically observed geometric surface and that the films of adsorbed argon were therefore actually only about $^1/_{20}$ as thick as he claimed. Presumably his method was not sufficiently sensitive to detect the formation of a few layers of adsorbed argon if, as in the case of potassium chloride, the total surface on which the adsorption could take place was the outer or geometric surface. A critical consideration of the polarization theory used by Bradley[12] will be reserved for another paper that is being written in collaboration with Dr. Edward Teller of George Washington University.

Summary

Low temperature van der Waals adsorption isotherms of some or all of the following gases have been determined on a variety of adsorbents at the temperatures indicated: argon and nitrogen

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(11) De Boer and Zwicker, *Z. physik. Chem.*, **B3**, 407 (1929).

(12) Bradley, *J. Chem. Soc.*, 1467 (1936).

at −195.8°; argon, nitrogen, carbon monoxide and oxygen at −183°; carbon dioxide at −78°; normal butane and sulfur dioxide at 0°. The following adsorbents have been used: two copper catalysts, glaucosil, pumice, nickel oxide supported on pumice, nickel on pumice, dry powdered bacteria, chromic oxide gel, "glowed" chromic oxide, potassium chloride, copper sulfate pentahydrate, anhydrous copper sulfate, two silica gel samples, activated charcoal, and two Darco samples (activated carbons). All adsorbents except charcoal gave S-shaped isotherms, and the values for the surface area evaluated from the different isotherms for the same adsorbent were consistent with each other.

WASHINGTON, D. C. RECEIVED OCTOBER 8, 1937

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, THE STATE UNIVERSITY OF IOWA]

Vapor Pressures and Partial Molal Volumes of Aqueous Solutions of the Alkali Sulfates at 25°[1]

BY J. N. PEARCE[2] AND H. C. ECKSTROM[3]

The vapor pressures of aqueous solutions of a number of electrolytes have been measured in this Laboratory. The data were used to calculate the thermodynamic functions useful in the study of solutions. Since all of the electrolytes previously studied had univalent anions, it seemed desirable to extend the measurements to electrolytes having divalent anions. For this purpose, the three most important alkali sulfates were chosen since the cations were common to many of the electrolytes previously studied.

The method used for measuring the vapor pressures was that developed by Pearce and Snow[4] with a few minor modifications mentioned in later publications by Pearce and students. The densities of the solutions were determined by means of a 100-ml. pycnometer.

The lithium, sodium and potassium sulfates of C. P. grade were recrystallized from distilled water and dried to constant weight. Solutions of the desired molality were made by adding the necessary weight of water to a known weight of anhydrous salt. The molality of the saturated solutions at 25° was determined gravimetrically by precipitating the sulfate ion as barium sulfate.

The vapor pressure data obtained are collected in Tables I, II and III. Column 4 contains values for $h/m^{1/2}$ where $h = (55.51 \ln a_1/\nu m) + 1$ and ν is the number of ions from one molecule of electrolyte. The values of the activity of the solvent, in column 5, have been calculated

TABLE I

VAPOR PRESSURES AND ACTIVITIES OF AQUEOUS SOLUTIONS OF LITHIUM SULFATE AT 25°

m	p_1, mm.	$(p_1^\circ - p_1)/p_1^\circ$	$h/m^{1/2}$	a_1	$\gamma_\pm$
0.0	23.752	0.0000	1.365	1.0000	1.000
.1	23.651	.0043	0.668	0.9958	0.445
.2	23.554	.0083	.502	.9917	.377
.4	23.360	.0165	.363	.9835	.321
.6	23.164	.0248	.293	.9752	.287
.8	22.962	.0333	.244	.9668	.272
1.0	22.757	.0419	.208	.9581	.260
1.5	22.220	.0645	.145	.9355	.246
2.0	21.646	.0887	.100	.9113	.241
2.5	21.071	.1129	.072	.8871	.240
3.0944[a]	20.363	.1427	.045	.8573	.241

[a] Saturated.

TABLE II

VAPOR PRESSURES AND ACTIVITIES OF AQUEOUS SOLUTIONS OF SODIUM SULFATE AT 25°

m	p_1, mm.	$(p_1^\circ - p_1)/p_1^\circ$	$h/m^{1/2}$	a_1	$\gamma_\pm$
0.0	23.752	0.0000	1.365	1.0000	1.000
.1	23.652	.0042	0.696	0.9958	0.433
.2	23.567	.0078	.616	.9922	.353
.4	23.393	.0151	.468	.9849	.283
.6	23.227	.0221	.401	.9779	.246
.8	23.072	.0286	.367	.9714	.221
1.0	22.927	.0347	.346	.9653	.200
1.5	22.565	.0500	.300	.9500	.166
1.9641[a]	22.239	.0637	.271	.9363	.145

[a] Saturated.

TABLE III

VAPOR PRESSURES AND ACTIVITIES OF AQUEOUS SOLUTIONS OF POTASSIUM SULFATE AT 25°

m	p_1, mm.	$(p_1^\circ - p_1)/p_1^\circ$	$h/m^{1/2}$	a_1	$\gamma_\pm$
0.0	23.752	0.0000	1.365	1.0000	1.000
.1	23.656	.0040	0.791	0.9960	0.419
.2	23.565	.0076	.625	.9923	.322
.4	23.399	.0149	.486	.9851	.257
.6	23.239	.0216	.422	.9784	.208
.6889[a]	23.172	.0244	.405	.9756	.196

[a] Saturated.

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(1) Part of the dissertation presented to the Graduate College of the State University of Iowa by Hartley C. Eckstrom in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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(4) Pearce and Snow, *J. Phys. Chem.*, **31**, 281 (1927).