first discontinuity with respect to water content, considering the 4% point as the lowest percentage water content gel obtainable without destruction of gel activity. Calculating the area covered by 0.04 g. of water one molecule thick also gives a value of about 1 × 10^6 sq. cm.

Summary

1. An adsorption-desorption curve of water vapor on silica gel showing no hysteresis was obtained.

2. The activity was evaluated for gels of varying water content as heat of wetting measurements.

3. A maximum in the heat of wetting determinations at a water content of 4% for this particular silica gel was observed.

4. The activation of the gel must be carried out in a manner that the water on the gel is evenly distributed over the surface or at least is in a state of equilibrium with the gel surface energy.

5. Silica gel can be most highly activated by holding it in a vacuum at 260 to 275° for many hours.

EAST LANSING, MICH. RECEIVED APRIL 10, 1937

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

The Use of Low Temperature van der Waals Adsorption Isotherms in Determining the Surface Area of Iron Synthetic Ammonia Catalysts

BY P. H. EMMETT AND S. BRUNAUER

In a recent communication[1] we published some low temperature physical adsorption isotherms for various gases on a pure iron synthetic ammonia catalyst and pointed out that they appeared to afford a means for calculating the surface area of the catalyst. Similar isotherms have now been determined for a total of six iron synthetic ammonia catalysts. The present paper gives the detailed experimental results that have been obtained and includes in addition a discussion of the various factors involved in interpreting the isotherms in terms of relative and absolute catalyst surface areas.

Experimental

The following six iron synthetic ammonia catalysts have been used: catalyst 930, containing 1.07% K_2O; 931, 1.59% K_2O and 1.3% Al_2O_3; 954, 10.2% Al_2O_3; 424, 1.03% Al_2O_3 and 0.19% ZrO_2; 958, 0.35% Al_2O_3 and 0.08% K_2O; and two different samples of an unpromoted iron catalyst 973 containing 0.15% Al_2O_3 as impurity. In the course of the work isotherms of some or all of the following gases have been determined on the various catalysts at the indicated centigrade temperatures: nitrogen and argon at −195.8°; nitrogen, argon, carbon monoxide and oxygen at −183°; methane and nitric oxide at −140°; nitrous oxide and carbon dioxide at −78°; ammonia at −36° and *n*-butane at 0°.

The adsorption apparatus, the general procedure used, the composition and reduction schedule of five of the catalysts, the nature of the −183 and −78° baths and the preparation and purification of the hydrogen, carbon monoxide and dioxide, nitrogen and helium have been described in a preceding paper.[2] The sixth catalyst (424) was reduced for forty-eight hours at 450° and forty-eight hours at 500°. Tank butane from the Ohio Chemical Company was condensed in a liquid air trap and the non-condensable gases were removed by pumping. Part of the remaining liquid was then vaporized into a storage bulb at room temperature. Tank oxygen containing 1.5 to 3% nitrogen was used for most of the runs; for one experiment pure electrolytic oxygen was used in place of tank oxygen to show that the small percentage of nitrogen did not materially alter the shape of the low temperature oxygen isotherm. Methane was obtained through the courtesy of the Heat Division of the National Bureau of Standards. It was condensed in a liquid air trap and degassed before using. Ammonia was taken from a tank of synthetic ammonia, dried over potassium hydroxide and used without further purification after it had been shown to contain a negligible quantity of non-condensable gas. For our supply of nitric oxide we are indebted to Dr. E. Melvin of this Laboratory who prepared it from sulfuric acid and sodium nitrite according to the method described by Noyes.[3] It contained no appreciable non-condensable gas; traces of nitrogen dioxide and water were removed by adsorption on glaucosil. Nitrous oxide from a tank was frozen in a liquid air trap and, after the removal of all non-condensable gas, vaporized from a −78° bath directly into the adsorption apparatus. Argon of 99.9% purity was used after being dried by passage through a −78° bath.

The −195.8° bath consisted of tank nitrogen that had been liquefied in fresh liquid air at about 35 pounds gage pressure. The tank nitrogen contained about 1% oxygen. For obtaining a temperature of −36° a liquid ammonia bath was used. A temperature of −140 ± 0.2° was obtained with a hand regulated thermostat; petroleum ether was used as a bath liquid. Cooling was obtained by liquid air. Sufficient stirring was provided by a stream of dry nitrogen bubbling through the bath to keep the temperature gradient throughout the bath smaller than 0.05°.

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

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

(3) W. A. Noyes, *ibid.*, **47**, 2170 (1925).

Whenever either chemical reaction, activated adsorption, or chemisorption of the reactants was found to occur at the temperature, T_1, at which the physical adsorption isotherm was to be measured, it was necessary before making the physical adsorption run first to saturate the catalyst with the particular gas at T_1 and then to remove from it all of the physically adsorbed but none of the chemically adsorbed gas by evacuating for a sufficient time at some suitable higher temperature T_2. For carbon monoxide runs T_1 was −183°, and T_2 −78°; for carbon dioxide T_1 was −78°, and T_2, 0°, though evacuation at 100° was employed in some of the carbon dioxide runs. In most of the carbon monoxide and carbon dioxide experiments the total gas taken up by the catalyst (sum of physical and chemical adsorption) was also measured. The difference between this total adsorption and the final physical adsorption is interpreted throughout the present paper as a measure of the chemisorption. The total adsorptions of carbon monoxide or of carbon dioxide when shown are designated by dashed curves in Figs. 1 to 10. Only for argon, nitrogen, butane, methane and probably ammonia (at −36°) were no chemisorptions or reactions encountered.

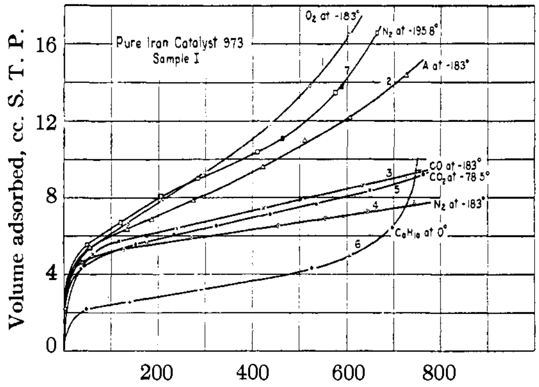

Fig. 1.—Low temperature adsorption isotherms for Catalyst 973 Sample I.

The gas contained in the "dead space" around the catalyst was corrected when necessary for deviations from the perfect gas laws. The percentage deviations used were as follows: nitrogen at −195.8°, 5%, and at −183°, 2.87%; oxygen at −183°, 3.17%; argon at −195.8°, 8.7%, and at −183°, 3.00%; carbon monoxide at −183°, 2.68%; methane at −140°, 5.92%; nitric oxide at −140°, 4.0%; nitrous oxide at −78°, 5.84%; carbon dioxide at −78°, 2.09%, and at 25°, 0.58%; ammonia at −36°, 2.64%, and at 25°, 1.185%; *n*-butane at 0°, 10.8%, and at 25°, 3.2%. All deviations refer to 760 mm. pressure, and all were assumed to vary linearly with pressure. The values for oxygen, nitrogen, argon and carbon monoxide at −183° and for carbon dioxide at −78° were very kindly furnished to us by Dr. A. F. Benton of the University of Virginia. The other values were obtained from the literature, most of them from the "International Critical Tables." The deviation for butane at 0 and 25° was from an article by Dana, Jenkins, Burdick and Timm.[4] The deviations for argon at −195.8° and for nitric oxide at −140° were estimated by comparison with other similar gases. However, in these two cases the adsorption was measured only on catalyst 954 which has a very large adsorption; therefore, even a two-fold error in the estimated percentage deviation would not appreciably affect the isotherms.

Results

Pure Iron Catalyst 973.—Sample I was used only after it had reached a constant and reproducible adsorptive capacity by being sintered up to 500°. The isotherms in Fig. 1,[5] and in each figure throughout the paper, are numbered in the relative order in which they were performed. The volume of carbon monoxide chemisorbed[6] at −183° was 5.5 cc.; at −78°, 6.0 cc. However, this catalyst while standing overnight in carbon monoxide at room temperature picked up a total of 15.4 cc. (9.4 cc. more than at −78°). After being freed from gaseous carbon monoxide by pumping at 0°, the catalyst bulb when rapidly heated to a few hundred degrees centigrade became coated on the inside with an iron mirror. From this observation, together with the experiments of Stoffel[7] one may conclude that the excess carbon monoxide picked up by the catalyst during the sixteen-hour exposure at room temperature was probably in the form of iron carbonyl.

Adsorption measurements for the oxygen isotherm were made after about 25 cc. of the gas had been picked up irreversibly and instantaneously by the catalyst at −183°. At −78° an additional 20 cc. of oxygen was quickly taken up. No measurable amount of slow sorption of oxygen occurred at either −183 or −78°. One experiment at −183° in which oxygen was added to the catalyst in successive small amounts and in the presence of a few mm. of helium gave approximately the same 25-cc. sorption of oxygen that was obtained in the absence of helium, indicating that the large oxygen pickup was not due to a sudden heating of the catalyst resulting from the first small amount of oxygen admitted. The maximum amount of the two kinds[8] of activated adsorption of hydrogen that we were able to obtain on sample I was 5.94 cc.

The second sample of 973 was reduced during ninety-six hours of exposure to a maximum temperature of 400°. Its surface is more than twice as great as that of the highly sintered sample I. The isotherms for this sample are shown in Fig. 2. The carbon monoxide runs indicated a chemisorption of 15.5 cc. at −183° and 18.2 cc. at −78°; an additional 1 cc. of irreversible adsorption occurred while the physical adsorption isotherm was being determined at −78°.

The presence of about 1.7 cc. of irreversible carbon di-

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(4) Dana, Jenkins, Burdick and Timm, *Refrigerating Eng.*, **12**, 387 (1936).

(5) The oxygen isotherm for pure iron catalyst 973 shown in Fig. 1 has been calculated from the experimental data with the help of the value furnished by Dr. Benton for the deviation of oxygen from the perfect gas laws at −183° (3.17% at −183°). The oxygen isotherm calculated for this catalyst and published in a previous article[1] was in error owing to the fact that an incorrect value for the density of oxygen gas at 760 mm. and −183° (4.74 g. per liter) was obtained from the "International Critical Tables," Vol. III, page 204, and used in calculating the "dead space" correction for the oxygen run.

(6) See ref. 2 for a detailed discussion of this chemisorption.

(7) Stoffel, *Z. anorg. Chem.*, **84**, 56 (1913).

(8) Emmett and Harkness, This Journal, **57**, 1631 (1935).

oxide adsorption at −78° on sample II of this catalyst has already been pointed out.[2]

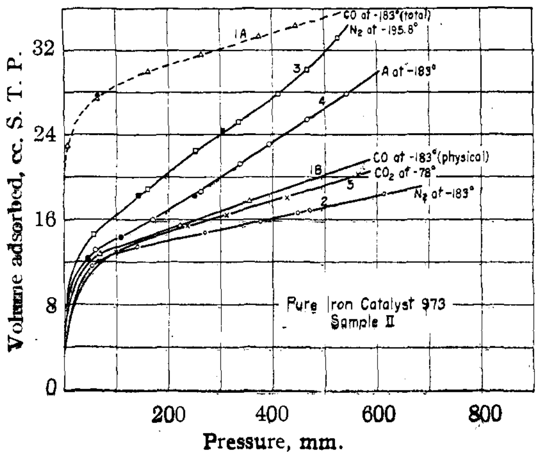

Fig. 2.—Low temperature adsorption isotherms for Catalyst 973 Sample II.

Singly Promoted Iron Catalyst 954 (10.2% Al_2O_3).—The constancy of the adsorptive capacity of this reduced catalyst is shown by the agreement between the two nitrogen runs at −183°, these being the first and thirteenth runs made on this sample of catalyst (Fig. 3). The chemisorption of carbon monoxide at −183° amounted to about 50 cc. and at −78°, 58 cc.; the irreversible adsorption of hydrogen at −78° was about 68 cc.

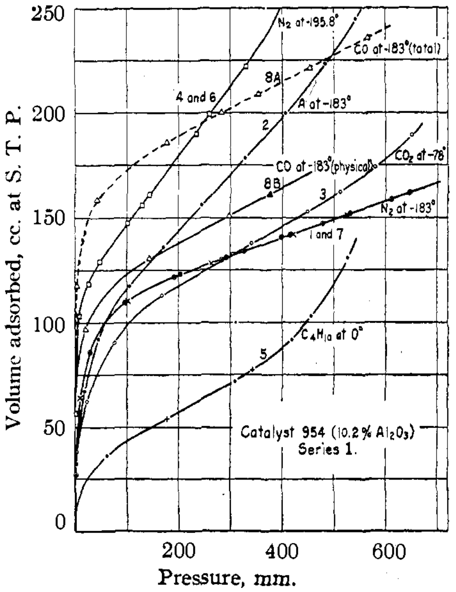

Fig. 3.—Low temperature adsorption isotherms for Catalyst 954 Series I.

While seeking some other gas which might undergo an instantaneous low temperature irreversible adsorption similar to that of carbon monoxide and thus serve as an added criterion for the amount of gas needed for a monolayer, an experiment with nitrous oxide was tried at −78°. It was soon found, however, that at this temperature nitrous oxide reacts with the iron with the liberation of free nitrogen, the oxygen remaining on the iron. It was therefore necessary first to saturate the surface with respect to oxygen before obtaining a physical adsorption isotherm for nitrous oxide. In carrying out this saturation process oxygen was added to the catalyst at −183°, though the catalyst was not cooled in helium from room temperature and might have been intermediate in temperature between −183 and 0°, when the first oxygen was added. In all, about 520 cc. of oxygen was taken up irreversibly by the catalyst. The van der Waals adsorption isotherm for nitrous oxide at −78° on the oxygen-covered catalyst is shown in Fig. 4, as is also one for nitric oxide at −140°. A nitrogen isotherm made at −183° after again reducing the catalyst following these two runs showed that some decrease in sorptive capacity occurred. The nitrous oxide and nitric oxide curves are probably to be compared with this new nitrogen isotherm rather than with the ones shown in Fig. 3.

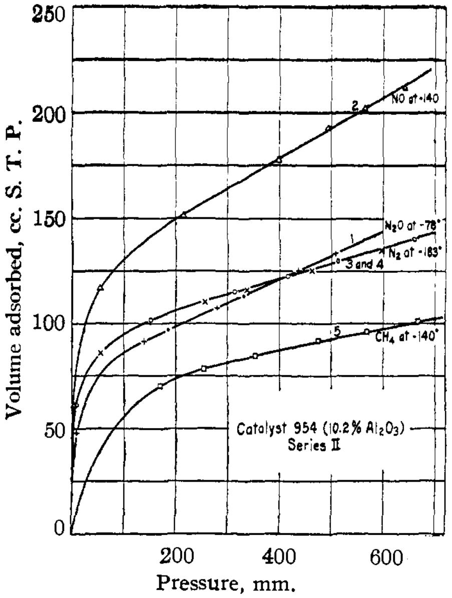

Fig. 4.—Low temperature adsorption isotherms for Catalyst 954 Series II.

An attempt to get isotherms for the total physical and chemical adsorption of nitric oxide at −140° on the reduced catalyst and then to differentiate between the two by pumping off all of the physical adsorption at −78° was frustrated by reaction between the nitric oxide and the iron at −78° to form iron oxide and nitrogen. Even at −140° an irreversible "creep" amounting to 15 cc. occurred while attempting to obtain the isotherm for the combined physical adsorption and chemical adsorption. Since the experiments at −140° could be made significant only by determining by frequent gas analysis whether or not reaction was occurring with the evolution of free nitrogen, the work on nitric oxide was abandoned temporarily after a few preliminary runs.

A carbon dioxide isotherm made several months after the methane isotherm of Fig. 4 showed that about 5 cc. of the carbon dioxide that is adsorbed at −78.5° would not pump off in one-half hour either at 0 or 100°.

Doubly Promoted Catalyst 931 (1.59% K_2O, 1.3% $Al.O_3$).—The experiments on doubly promoted catalyst 931 can be divided conveniently into three groups. The first of these comprises a series of isotherms taken after the catalyst had been sintered gradually up to 530° and then, after an accidental break in a glass connecting tube with resulting partial oxidation of the catalyst, finally reduced at 450°. The isotherms for this group of runs are shown in Fig. 5. Attention has already been called[2] to the fact that the carbon dioxide isotherms indicate a large chemisorption of carbon dioxide on this catalyst.

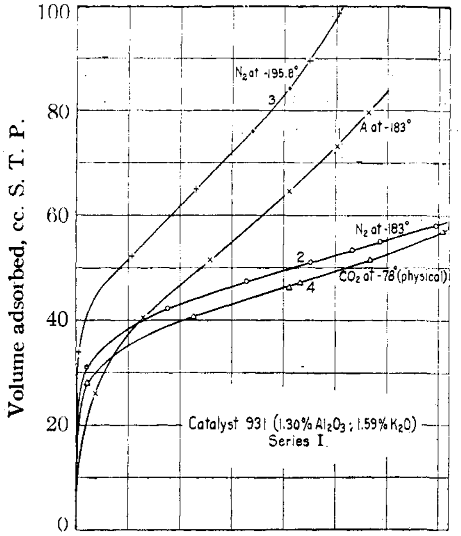

Fig. 5.—Low temperature adsorption isotherms for Catalyst 931 Series I.

The second group of runs was made after the catalyst had been sintered for seven hours at 575°. The isotherms are shown in Fig. 6. The chemisorption of carbon monoxide amounted to 10.6 cc. at −183° and 14.7 cc. at −78°. The oxygen isotherm was obtained after saturating with oxygen at −78°, 152 cc. of oxygen being taken up at that temperature before the isotherm at −183° was obtained. The third group of runs (Fig. 7) was taken after the catalyst had sintered a little more as a result of being partially oxidized and reduced several times at 450°. The ammonia isotherm at −36° appeared to represent physical adsorption. However, increasing the temperature to 100° revealed definite reaction of the ammonia with the iron, 5.8 cc. of hydrogen being removed from the catalyst dead space after one and one-half hours' exposure. In view of this behavior of ammonia with iron, it was not considered worth while to attempt to prove what fraction of the −36° adsorption may have been of the activated type. The largest activated adsorption of hydrogen obtained on catalyst 931 was about 20 cc. It was measured at −183° after letting the catalyst stand in hydrogen for fifteen minutes at 350° and then overnight at room temperature. This hydrogen adsorption was made when the nitrogen adsorption capacity was that shown in the nitrogen isotherm in Fig. 6.

Doubly Promoted Catalyst 958 (0.35% Al_2O_3, and 0.08% K_2O).—Catalyst 958 was selected with a view to obtaining one with as small an amount of promoter as would assure a fairly large and reproducible surface. The isotherms are shown in Fig. 8. The carbon monoxide isotherm at −183° illustrates particularly well the characteristics of the chemisorption of carbon monoxide by iron at this low temperature. The first point on the isotherm corresponds to a steady adsorption value reached fifteen minutes after admission of the carbon monoxide; however, within two minutes of the time of admission all but 1 cc. of the final 19 cc. of chemisorption had taken place. At −78.5° the chemisorption was 21.5 cc. The chemisorption of carbon

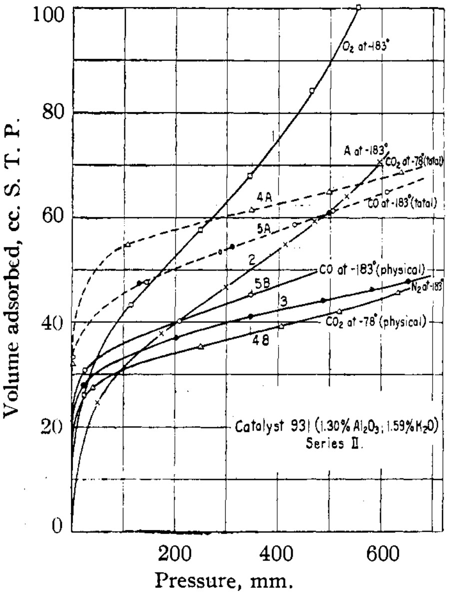

Fig. 6.—Low temperature adsorption isotherms for Catalyst 931 Series II.

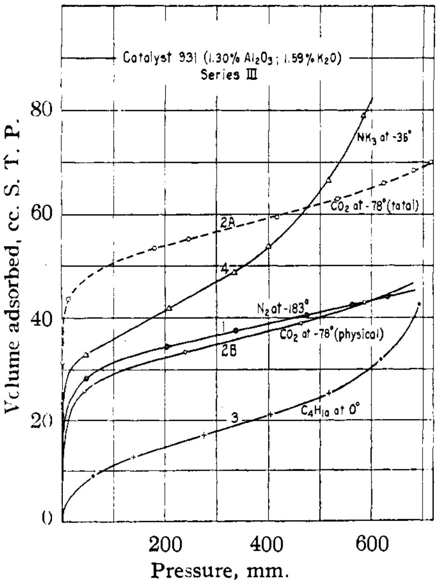

Fig. 7.—Low temperature adsorption isotherms for Catalyst 931 Series III.

dioxide on this catalyst was between 5 and 8 cc. The largest activated adsorption of hydrogen was 16.2 cc.; this was obtained at −78°, though the catalyst had stood in hydrogen at room temperature for two days during part of the run.

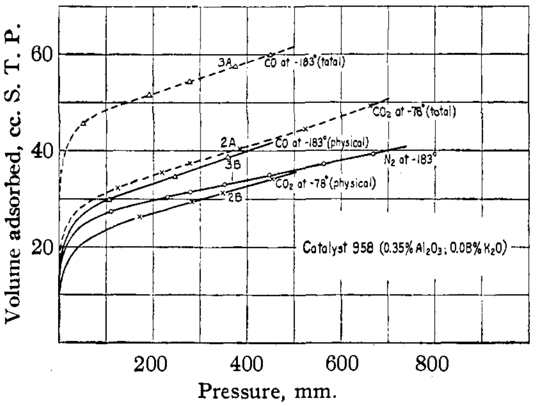

Fig. 8.—Low temperature adsorption isotherms for Catalyst 958.

Singly Promoted Catalyst 930 (1.07%[9] K_2O).—The isotherms are shown in Fig. 9. The portion of the chemisorption of carbon dioxide that was not removed during one-half hour evacuation either at 0 or 100° amounted to about 4.2 cc., as is evident from a comparison of the total adsorption isotherm with the isotherm for the physical adsorption. Similarly, the volume of chemisorbed carbon monoxide not removed by one-half hour evacuation at −78° was 2.4 cc.

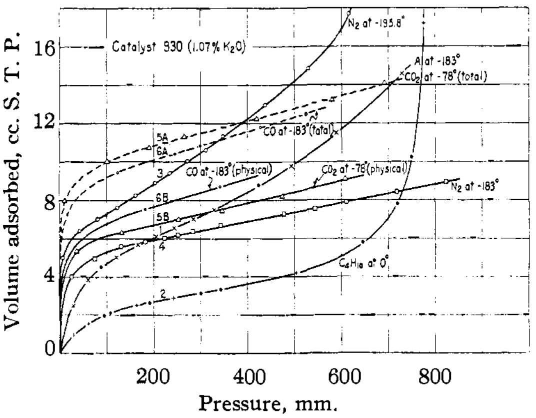

Fig. 9.—Low temperature adsorption isotherms for Catalyst 930.

Catalyst 424 (1.03% Al_2O_3 and 0.19% ZrO_2).—In the isotherms for catalyst 424 shown in Fig. 10 the total carbon monoxide adsorption is indicated by the dashed line. On the other hand, for carbon dioxide the isotherm for total adsorption is shown by a solid line since only a single point was taken on the physical adsorption curve after evacuating for half an hour at 0°. This one point indicates that no more than 8 cc. of the total carbon dioxide adsorption was chemisorption.

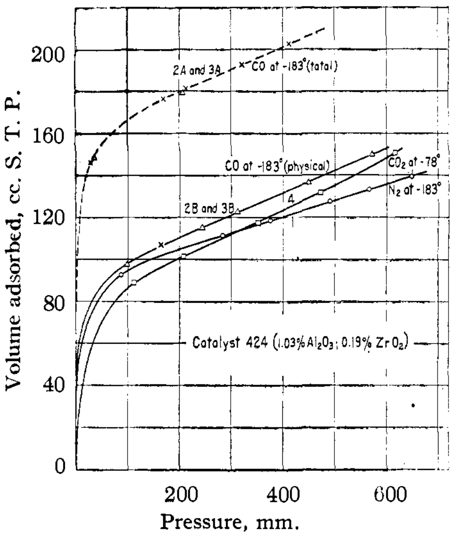

Fig. 10.—Low temperature adsorption isotherms for Catalyst 424.

Discussion

A cursory examination of the isotherms included in Figs. 2 to 10 suffices to show that the curves have the same general characteristics noted in a previous publication[1] for the low temperature isotherms on sample I of pure iron catalyst 973 (Fig. 1). Each isotherm may be described as an S-shaped curve, the central portion of which is linear over a considerable pressure range within experimental error. The linear portion of isotherms of gases whose molecules are of about equal size here, as in the case of the pure iron catalyst, converge toward an approximately common point at low pressures in a manner that strongly suggests their usefulness for measuring the absolute and relative surface areas of iron catalysts.

For the pure iron catalyst, on the assumption that the linear portion of the isotherms represented the pressure region in which a second layer of adsorbed molecules was being built up, we previously recommended the selection of the intercept of the extrapolated linear part of the isotherm with the volume axis as the point corresponding to the volume of gas required to form a monomolecular layer on the catalyst surface (point A, Fig. 11). It seems, however, that point B, the actual juncture of the low pressure extremity of the linear part of the isotherms with the low pressure curved region is *a priori* fully as logical a

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(9) As reported in a previous paper[2] analysis of the white coating present on the inside of two different catalyst bulbs after reduction of the catalyst showed that about 60% of the alkali content of the catalyst had evaporated and condensed on the glass wall; hence, the catalyst really contained only about 0.5% K_2O during the adsorption runs.

choice for a monomolecular layer as point A even when the linear portion is interpreted as the building up of a second layer. Furthermore point C, the mid-point of the linear part of the isotherm, might be construed as marking the completion of a monolayer if the curves are considered as smooth S-shaped curves, and the actual linear portion as being really infinitesimal in length and located at the point of inflection between the two curved extremities of the isotherms.

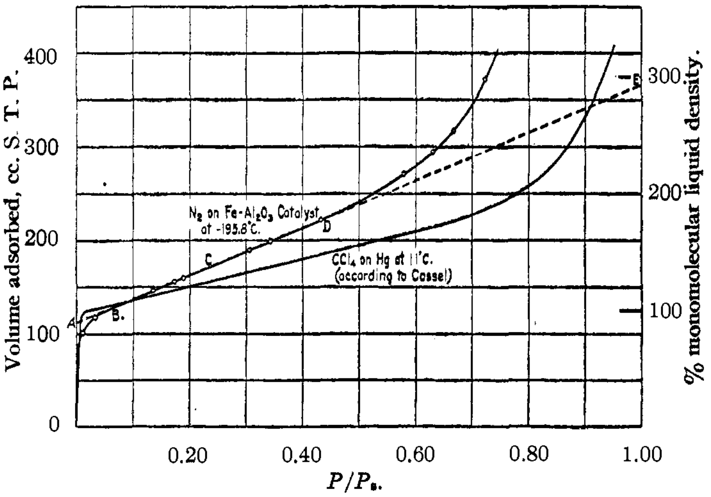

Fig. 11.—A comparison between an adsorption isotherm for nitrogen at −195.8° obtained on iron Catalyst 954 and the adsorption isotherm for carbon tetrachloride on liquid mercury calculated by Cassel[11] from his measurements of the effect of carbon tetrachloride vapor on the surface tension of mercury.

In the absence of any well founded theoretical equation for explaining the shape of the low temperature physical adsorption isotherm, it becomes necessary to rely upon the experimental physical and chemical adsorption data in attempting to ascertain the volume of gas required to form a monomolecular layer on the iron catalysts. It seems desirable, furthermore, to make at the start no assumptions as to the significance of the linear portion of the isotherm. Accordingly we shall now consider the adsorption data in order to determine within what limits it seems possible at present to specify the volume of gas required to form a monomolecular layer on the catalysts and to designate the absolute surface area in each instance. For completeness we shall include in our discussion points D and E shown for the nitrogen isotherm in Fig. 11. These represent, respectively, the high pressure limit of the linear portion and the intercept of the latter on extrapolation to the saturation pressure P_s. Neither of these points appears to be a likely choice as a monomolecular layer though it is possible that each might correspond to definite multiples of the volume of gas required for a monomolecular layer.

The calculation of the surface area that could be covered by the volumes of gas corresponding to points A, B, C, D, and E merely consists of the multiplication of the number of molecules in each volume by the average area that each molecule would occupy when adsorbed on the catalyst surface. This latter quantity must depend essentially on the molecular diameters used in the calculation. If one assumes that the average cross section of the adsorbed molecules is the same as that corresponding to the plane of closest packing in the solidified gas one obtains the area occupied by each adsorbed molecule on the surface, Area (*S*), from the equation

$$\text{Area }(S) = (4)(0.866)\,(M/4\sqrt{2}\,AD_s)^{2/3}$$

where M is the molecular weight of the gas, D_s is the density of the solidified gas and A is Avogadro's number. The molecular areas can also be calculated from the average space occupied by each molecule in the liquefied gas by substituting the density of the liquefied gas D_l for D_s in the above equation. Close packing of the physically adsorbed molecules is uniformly assumed. In Table I are shown the numerical values of "area (*S*)" and "area (*L*)" used throughout the present paper and the data from which they were derived.

The volumes of the various gases corresponding to points A, B, C, D, and E on the physical adsorption isotherms of Figs. 1 to 10 are summarized in Table II. Also, the areas equivalent to such volumes of physically adsorbed molecules are listed, both for area (*S*) and area (*L*) values per molecule. For carbon monoxide and nitrogen at −183°, nitric oxide and methane at −140°, and nitrous oxide at −78° adsorptions were not obtained at pressures above those for the linear part of the isotherms; in these instances, therefore, points C and D cannot be determined.

In comparing the data for points A, B, C, D, and E in Table II it is well to bear in mind that the particular point that really represents the completion of a monomolecular layer (or *n* times a monomolecular layer) probably ought to yield about the same numerical value for the area when

TABLE I

AREA OCCUPIED BY EACH ADSORBED MOLECULE

Gas	Density of solidified gas, g./cc.	Temp., °C.	Area (S), Å.²	Density of liquefied gas, g./cc.	Temp., °C.	Area (L), Å.²
N_2	1.026[a]	−252.5	13.8	0.751[a]	−183	17.0
				0.808[a]	−195.8	16.2
O_2	1.426[a]	−252.5	12.1	1.14[a]	−183	14.1
A	1.65[a]	−233	12.8	1.374[a]	−183	14.4
CO	[b]	−252.5	13.7	0.763[a]	−183	16.8
CO_2	1.565[a]	− 80	14.1	1.179[a]	− 56.6	17.0
CH_4	[c]	−253	15.0	0.3916[a]	−140	18.1
C_4H_{10}	[d]		32.0	0.601[a]	0	32.1
NH_3	[e]	−80	11.7	0.688[a]	− 36	12.9
NO	[f]			1.269[a]	−150	12.5
N_2O	[g]		14.4	1.199[a]	− 80	16.8

[a] "International Critical Tables," Volume III. [b] Edge of unit cube of α-CO = 5.63 Å. at −252.5°; face centered; Wyckoff, "The Structure of Crystals" (second edition), p. 224. [c] Edge of unit cube = 5.89 Å.; face centered; Wyckoff, "The Structure of Crystals," (supplement to the second edition), p. 136. [d] It was assumed that the butane molecule lies flat on the surface; an oblong was assigned to each molecule with one side 4.3 Å., the other 7.45 Å. These values were calculated on the basis of S. B. Hendricks, *Chem. Rev.*, **7**, 431 (1930). [e] Edge of unit cube = 5.19 Å. at −80°; face centered; Wyckoff, "Structure of Crystals," (second edition), p. 260. [f] No data available in literature. [g] Edge of unit cube = 5.77 Å.; face centered; Wyckoff, "The Structure of Crystals" (second edition), p. 238.

calculated from one gas as from another. However, until restricted by other considerations, n may have any value. Accordingly, approximate agreement among the areas calculated from different gases for a particular point is a probable prerequisite for, but not a sufficient proof of, that point corresponding to a monomolecular layer.

A comparison of the areas calculated for the gas volumes at points A, B, C, D, and E on each of the catalysts reveals that somewhat better agreement is obtained for point B than for any of the other points. One representative way of comparing the data will suffice as an illustration. The average value of the area calculated for point B on the isotherms for catalyst 973-I is 20.3 sq. meters per 25-cc. sample (using area (S) values per molecule); the maximum deviation of the surface area calculated from any one isotherm for this point is about 12% of this average value. Such maximum deviations for all the catalysts for point B are between this value[10] and 3%. For point A analogous maximum deviations range from 7 to 28.4%; for point C, from 5 to 17%; for D, from 7 to 20%; and for E from 11 to 27% if all isotherms are included, but from 5 to 11% if the carbon dioxide isotherms and the single ammonia run are omitted. If area (L) values are used for the various gases in making the above comparisons, the areas for point B still agree more closely than for any of the other points, though the margin of superiority over points C and D is rather small. Furthermore, the maximum deviations are somewhat larger when using area (L) than when using area (S) values for molecular cross section.

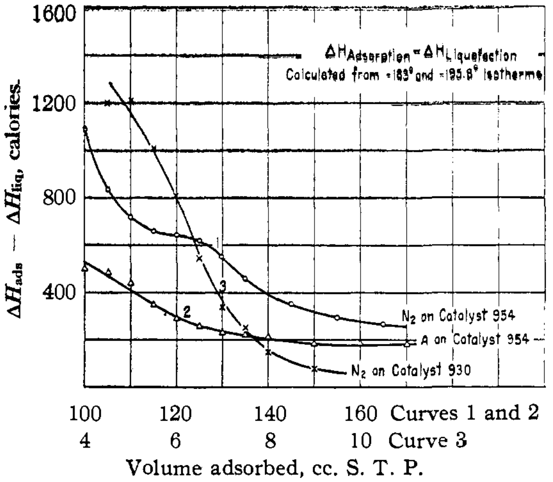

Fig. 12.—Variation of $\Delta H_{\text{adsorption}} - \Delta H_{\text{liquefaction}}$ with volume adsorbed for nitrogen on Catalysts 954 and 930, and for argon on Catalyst 930 (calculated from −183 and −195.8° isotherms).

Perhaps an even greater contribution of the physical adsorption data toward indicating the volume of physically adsorbed gas required for a monomolecular layer becomes apparent when the differential heats of adsorption are calculated. In Fig. 12 are curves showing the amount by which the calculated heats of adsorption of nitrogen and of argon on two of the catalysts exceed

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(10) The carbon monoxide run on catalyst 930 is omitted in taking the averages here referred to because we believe that the so-called physical adsorption for carbon monoxide (curve 6B, Fig. 9) actually includes several cc. of chemisorbed carbon monoxide. Our reason for so believing is that for catalyst 930 the volume of carbon monoxide for point B on the physical adsorption isotherm is 20 to 25% greater than the volume of nitrogen, whereas on each of the five other iron catalysts point B corresponds to about equal volumes of carbon monoxide and of nitrogen. Since inclusion of the isotherms for the physical adsorption of oxygen, carbon monoxide, and carbon dioxide is warranted only in those instances in which a temperature of evacuation can be found for each gas and catalyst such that all physical adsorption but none of the chemical adsorption can be removed, the omission of the carbon monoxide isotherm for 930 from the area calculations for the present seems not only permissible but imperative. Though it is too early to predict with certainty the distribution of the chemisorbed carbon monoxide between the iron atoms and the surface alkali molecules of catalyst 930, it seems fairly certain that some of the chemisorbed carbon monoxide is taken up by the alkali at −183°. This is in marked contrast to the behavior of catalysts 931 and 958 containing K_2O-Al_2O_3 or of catalysts 954 and 424 containing only Al_2O_3 in all of which the carbon monoxide appears to be chemisorbed only by the iron atoms and not by the promoter molecules on the surface of the catalysts.[3]

TABLE II

ADSORPTION VOLUMES AND EQUIVALENT AREAS FOR POINTS A, B, C, D, AND E ON THE ISOTHERMS OF FIGS. 1 TO 10

Gas	Temp., °C.	Point A			Point B			Point C			Point D			Point E		
		Vol., cc.	Area (*L*), sq. m.	Area (*S*), sq. m.	V 1., cc.	Area (*L*), sq. m.	Area (*S*), sq. m.	Vol., cc.	Area (*L*), sq. m.	Area (*S*), sq. m.	Vol., cc.	Area (*L*), sq. m.	Area (*S*), sq. m.	Vol., cc.	Area (*L*), sq. m.	Area (*S*), sq. m.
A. Unpromoted Iron Catalyst 973; Sample I. (0.15% Al_2O_3 impurity). Weight[a] 63.4 grams																
N_2	−195.8	4.8	21.0	17.9	5.5	24.1	20.5	6.9	30.2	25.8	8.3	36.4	31.0	17.1	74.8	63.8
N_2	−183	4.95	22.8	18.5	5.5	25.3	20.5							15.1	69.4	56.4
A	−183	4.9	19.1	17.0	5.8	22.6	20.1	7.55	29.4	26.1	9.3	36.2	32.2	16.1	62.6	55.8
CO	−183	5.1	23.2	18.9	5.7	25.9	21.1							15.4	70.0	57.0
CO_2	− 78	4.85	22.3	18.5	5.95	27.4	22.7	7.2	33.1	27.5	8.4	38.6	32.0	12.5	57.4	47.6
C_4H_{10}	0	2.0	17.4	17.3	2.2	19.1	19.0	3.1	26.9	26.8	4.0	34.7	34.6	5.3	46.0	45.8
O_2	−183	4.5	17.2	14.7	5.5	21.0	18.0	7.75	29.6	25.4	10.0	38.1	32.7	16.9	64.4	55.4
B. Unpromoted Iron Catalyst 973; Sample II. (0.15% Al_2O_3 impurity). Weight[a] 67.0 grams																
N_2	−195.8	12.5	54.8	46.7	14.5	63.5	54.1	18.3	80.2	68.3	22.1	96.8	82.2	43.1	189	161
N_2	−183	11.9	54.7	44.4	13.2	60.7	49.3							41.4	190	154
A	−183	11.4	44.4	39.5	13.2	51.4	45.7	15.9	61.9	55.0	18.6	72.4	64.4	39.0	152	135
CO_2	− 78	12.0	55.2	45.8	14.2	65.2	54.2	16.7	76.8	63.7	19.2	88.2	73.2	32.2	148	123
CO	−183	11.8	53.6	43.7	13.2	60.0	48.9							42.2	192	156
C. Singly Promoted Catalyst 954; (10.2% Al_2O_3); Weight[a] 66.8 grams. Series I.																
N_2	−195.8	113.5	497	424	128	560	478	175.5	768	655	223	977	832	364	1594	1358
N_2	−183	105	483	392	121	556	452							348	1600	1298
A	−183	90.5	352	313	128	499	443	164	639	568	200	779	692	361	1406	1250
CO_2	− 78	89	409	340	110	506	420	135	620	515	160	736	610	290	1332	1106
CO	−183	111.5	496	413	130	578	482							352	1564	1304
C_4H_{10}	0	29.5	256	255	50	434	433	63.5	551	550	77	668	666	139	1208	1202
D. Singly Promoted Catalyst 954; Series II.																
N_2	−183	92	423	343	108.5	499	405							296	1360	1104
NO	−140	120.5	407		149	504								449	1516	
CH_4	−140	68.5	335	278	89	436	361							232	1136	942
N_2O	− 78	75.5	343	294	90	409	351							240	1090	934
E. Doubly Promoted Catalyst 931; (1.30% Al_2O_3, 1.59% K_2O); Weight[a] 61.0 grams. Series I.																
N_2	−195.8	41.6	182	155	46.4	203	173	61.4	269	229	76.4	335	285	119.6	524	446
N_2	−183	37.8	174	141	46.4	213	173							119.6	548	444
A	−183	29.8	116	103	41.0	160	142	53.5	208	185	66.0	257	229	114.6	446	396
CO_2	− 78	33.4	154	127	39.2	180	149	45.6	210	174	52.0	239	198	78.6	362	300
F. Doubly Promoted Catalyst 931; Series II.																
O_2	−183	31.4	120	103	42.0	160	137	55.0	210	180	68.0	259	222	112.0	428	366
N_2	−183	33.6	154	125	40.0	184	149							94.8	436	354
CO	−183	32.8	149	122	38.4	175	142							97.4	442	360
A	−183	25.4	99	88	38.0	148	132	49.5	193	171	61.0	238	211	96.8	378	336
CO_2	− 78	28.8	132	110	34.0	156	130	38.5	177	147	43.0	198	164	65.2	300	248
G. Doubly Promoted Catalyst 931; Series III																
NH_3	− 36	30.4	106	96	32.8	115	104	41.0	143	130	49.2	172	156	67.0	234	212
CO_2	− 78	27.2	125	104	31.8	146	121	35.4	163	135	39.0	179	149	63.0	290	240
N_2	−183	29.9	138	112	32.7	150	122							92.6	426	346
C_4H_{10}	0	8.4	73	73	12.8	111	111	17.0	148	148	21.2	184	184	33.0	286	286
H. Doubly Promoted Catalyst 958; (0.35% Al_2O_3, 0.08% K_2O); Weight[a] 71.6 grams.																
CO	−183	26.4	120	98	30.0	136	111							88.4	402	328
CO_2	− 78	21.4	98	82	26.0	120	99							61.4	282	234
N_2	−183	25.6	118	95	29.8	137	111							82.6	380	308
I. Singly Promoted Catalyst 930; (1.07% K_2O); Weight[a] 64.5 grams.																
N_2	−195.8	5.7	25.0	21.3	6.4	27.6	23.5	8.45	37.0	31.5	10.6	46.4	39.5	17.6	77.0	65.6
N_2	−183	5.0	23.0	18.7	5.7	26.2	21.3							18.4	84.6	68.6
CO_2	−78	5.6	25.8	21.4	6.1	28.0	23.3	7.4	34.0	28.2	8.7	40.0	33.2	14.5	66.6	55.2
C_4H_{10}	0	1.75	15.2	15.2	2.5	21.7	21.6	3.15	27.3	27.3	3.8	33.0	32.9	7.4	64.2	64.0
A	−183	3.85	15.0	13.3	5.7	22.2	19.7	6.7	26.1	23.2	7.7	30.0	26.7	18.5	72.0	64.0
J. Singly Promoted Catalyst 424; (1.03% Al_2O_3, 0.19% ZrO_2); Weight[a] 68.1 grams.																
N_2	−183	90.0	414	336	104	478	388							304	1398	1134
CO	−183	90.0	409	334	105.5	479	391							282	1280	1044
CO_2	− 78	78.5	361	299	98	450	374	117.5	540	448	137	630	522	241	1108	920

[a] The weights given in this table, as well as the percentages of promoters, refer to the unreduced catalysts. The weights of the iron itself in the seven catalysts were the following: Catalyst 973, Sample I—46.2 g.; Sample II—48.8 g.; Catalyst 954—43.6 g.; Catalyst 931—42.8 g.; Catalyst 958—54.5 g.; Catalyst 930—45.9 g.; and Catalyst 424—49.8 g.

the heats of liquefaction as a function of the volume of gas adsorbed. It is evident that on curve 1 for nitrogen on catalyst 954 there occurs a hump at a volume of about 125 cc. This is in remarkably close agreement with the 128 and 121 cc. corresponding to point B on the −195.8 and −183° isotherms, respectively. The other two curves are calculated from isotherms for which fewer experimental points are available. No hump is visible in either of them. Regardless of whether or not a hump is obtained, however, it is evident from the curves of Fig. 12 that at an adsorbed volume 25% larger than that for point B the calculated heat of adsorption is only 250 calories or so in excess of the heat of liquefaction of the gas whereas at a volume 25% smaller than for B the heat of adsorption is about 1000 calories greater than the heat of liquefaction. From all that is known about the relative values of heats of physical adsorption (in the first layer) and heats of liquefaction it seems safe to conclude that the former of these two points (25% above B) corresponds to adsorption in other than the first layer whereas the latter of the two (25% below B) corresponds to adsorption in the first layer. Accordingly, the physical adsorption data taken as a whole seem to indicate that not only is B a possible choice for the point corresponding to a monomolecular layer but the most probable of all five points as judged by the variation of the heat of adsorption with the volume adsorbed.

Turning now to a consideration of the various chemisorptions, we find that point B, and probably even point A, leads to a surface area that is apparently ample to accommodate the largest activated adsorption of hydrogen, and chemisorption of carbon monoxide that have been noted for pure iron catalyst 973, when due allowance is made for the probable difference in packing between molecules that are chemisorbed and those that are physically adsorbed on the surfaces. Thus the volume of carbon monoxide chemisorbed at −183° on sample I of pure iron catalyst 973 was practically the same as the volume of carbon monoxide adsorbed at point B on the physical isotherm and the maximum volume of activated adsorption of hydrogen was only 5% greater. For sample II the volumes of carbon monoxide chemisorbed at −183 and −78° were 13 and 33%, respectively, greater than point B on the physical adsorption isotherm for carbon monoxide at −183°. The possible densities of packing of chemisorbed carbon monoxide molecules on the iron are such that as much as 68% more chemisorbed carbon monoxide might be required for a monomolecular layer[11] than physically adsorbed carbon monoxide, each molecule of which is assumed to cover 13.7 sq. Å. (see Table I).

Although because of the above-mentioned uncertainty of packing density the chemisorption of carbon monoxide and the activated adsorption of hydrogen on pure iron catalyst 973 cannot accurately fix the point on the physical isotherms corresponding to a monomolecular layer, they do very definitely show that for the iron synthetic ammonia catalysts the physical adsorption at point B on the isotherms is approximately one layer in thickness rather than of the order of 20 layers claimed by Bradley[12] for similarly shaped isotherms of argon on copper sulfate and aluminum sulfate. Reserving for a future paper a critical discussion of the theory by which Bradley believes he can explain such thick films, we should like to point out that his conclusion as to the thickness of his films of adsorbed argon is based entirely upon his microscopic estimates of the diameters of the crystalline particles used. If, as seems probable, the crystals of copper sulfate and aluminum sulfate that Bradley prepared by dehydrating the hydrates were highly porous, the "internal" surface might be many times as large as the "external" surface. In such an event, the adsorption at the point on his isotherms corresponding to B might well correspond approximately to a monomolecular layer over the total (internal and external) surface rather than to a layer 20 molecules thick on the external surface.

Attention has already been called[2] to the fact that on promoted iron catalysts the chemisorption of carbon monoxide and the activated adsorption of hydrogen are both much smaller in comparison to the volume of physical adsorption needed for a monomolecular layer than on the pure iron catalysts; and that on all catalysts containing potassium oxide a considerable volume of carbon dioxide is chemisorbed at −78°. These facts have been interpreted as indicating that a

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(11) The calculation of the exact density of packing is rendered impossible by the lack of knowledge as to what planes of the iron crystals in the catalyst are exposed. Usually it is assumed that the developed faces are 100, 111, or 110 planes. The density of packing of the iron atoms in these three respective planes are such as to correspond to 8.14, 14.16, and 5.76 sq. Å. per iron atom. Of these values the 8.14 sq. Å. is probably the smallest that would permit one carbon monoxide molecule to be adsorbed on each iron atom. It was accordingly used in arriving at the 68% figure given above. If every face were a 111 plane, the volume of chemisorption for saturation would be 3% less than the physical adsorption; if only 110 faces existed, and one carbon monoxide molecule was held by each two iron atoms (2 × 5.76 = 11.52 sq. Å. per carbon monoxide molecule) the excess of chemisorbed carbon monoxide would be 19%.

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

large fraction of the surface of a doubly promoted iron catalyst is covered with the K_2O–Al_2O_3 promoter combination even though the catalysts as a whole contain only about 1% K_2O and 1% Al_2O_3. In an analogous manner the data in the present paper indicate that aluminum oxide promoters tend to accumulate on the surface of the iron catalysts. From a comparison of the curves (dashed) for the total carbon monoxide sorption in Figs. 3 and 10 with the curves for the physical adsorption it follows that the chemisorptions of carbon monoxide at −183° on singly promoted catalysts 954 (10.2% Al_2O_3) and 424 (1.03% Al_2O_3) are smaller than the volume of physically adsorbed carbon monoxide required for a monomolecular layer on the entire catalyst sample by 55 and 35%, respectively, indicating that at least these percentages of the surface are covered with aluminum oxide or some Al_2O_3–Fe compound that is not capable of chemisorbing CO.[13] The method yields results that are qualitatively similar to, but more susceptible of quantitative interpretation than those of Erofeev and Mochalov,[14] who concluded from some high frequency coherer experiments that "at the surface of a promoted iron catalyst there is a film of adsorbed aluminum oxide."

The one remaining irreversible gas sorption on the iron catalysts that should be mentioned is that of oxygen. The rapid taking up of oxygen by the catalysts at −183° is a curious phenomenon that merits further study. The experimental results cited in the present paper show that the various catalysts take up an amount of oxygen instantaneously and irreversibly at −183° that is five to ten times as great as the volume of carbon monoxide that they are capable of chemisorbing at −183°. Apparently, as one might expect, oxygen reacts with a number of layers of iron atoms to form a very thin film of one of the iron oxides. Nevertheless it is strange that the total irreversible sorption of oxygen at −183° should take place instantaneously at a fraction of a mm. pressure and should not be followed by any slower sorption during the subsequent determination of the isotherm for the physical adsorption of oxygen at pressures up to 760 mm. At −78°, oxygen sufficient to oxidize several additional layers of iron atoms is taken up and at this temperature, as at −183°, the sorption is practically instantaneous.

When all the physical and chemical adsorption data on the iron catalysts are taken into account it therefore seems that the following facts and correlations become evident. (1) A comparison of the areas equivalent to the gas volumes at points A, B, C, D, and E on each of the catalysts reveals that better agreement is obtained for point B than for any of the other points.

(2) Calculation of heats of adsorption by the Clapeyron equation from the nitrogen isotherms and the argon isotherms at −183 and −195.8° reveals that at a volume of adsorption corresponding to point B the heat of adsorption is intermediate between that expected for the adsorption in the first layer and the heat of liquefaction.

(3) The chemisorption of carbon monoxide at −183° and −78° and the activated adsorptions of hydrogen are consistent with the areas calculated from point B of the low temperature isotherms for pure iron providing reasonable assumptions are made as to the closeness of packing of the irreversibly adsorbed hydrogen and carbon monoxide.

It is to be noted that these correlations are arrived at without making any assumption as to whether the linear portion of the isotherms corresponds to the building up of a second layer of adsorbed molecules. They all combine to indicate, however, that point B marks approximately the completion of a first layer and that therefore the linear portion of the isotherms does indeed appear to be the region in which multiple layers of adsorption are building up. In this connection it may be well to cite one entirely different type of experiment that has yielded an adsorption isotherm similar to those shown in the present paper and that in a sense affords a precedent for the selection of the beginning of the linear portion of the isotherm as the point of completion of the first layer. Cassel[15] has published data from which he calculated the number of molecules of carbon tetrachloride adsorbed per square centimeter on a liquid mercury surface as a function of the pressure of carbon tetrachloride. The calculations were made by applying the Gibbs equation to measurements of the decrease in surface tension of the mercury with an increase in the partial pressure of the surrounding carbon tetrachloride

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(13) This decrease in the amount of chemisorption of carbon monoxide cannot be due to traces of alkali that might be present as impurities because the chemisorptions of carbon dioxide by these two catalysts are quite small, amounting to only 5 to 8% of the volume required for a monomolecular layer of physical adsorption.

(14) Erofeev and Mochalov, *Acta Physiochim. U. R. S. S.*, **4**, 861 (1936).

(15) Cassel, *Trans. Faraday Soc.*, **28**, 177 (1932).

atmosphere. On assigning to each adsorbed carbon tetrachloride molecule an area calculated from the density of liquid carbon tetrachloride he obtained the curve shown in Fig. 11. Included in the same figure is an isotherm that we have obtained for nitrogen on an iron synthetic ammonia catalyst at −195.8°. The similarity between the two curves is striking. The point of special interest for the present discussion, however, is the fact that the beginning of the linear portion of the carbon tetrachloride isotherm appears to correspond to the completion of a monomolecular layer of adsorbed molecules.

In summing up the discussion relative to the use of the low temperature adsorption isotherms for measuring the absolute surface areas of catalysts, we venture to estimate that on the basis of the experimental data here presented the volume of gas required for a monomolecular layer of physical adsorption is within ±15% of that corresponding to point B and that if the area occupied per adsorbed molecule is equal to area (*L*), area (*S*), or some value between these two, the absolute area of each of the iron synthetic ammonia catalysts is within ±25% of the average between the areas listed in the L and the S columns under point B in Table II. These estimates must, of course, be regarded as tentative though it is hoped that subsequent work will narrow and not widen the limits of uncertainty.

Thus far the discussion has been restricted almost entirely to a consideration of *absolute* surface areas. From the data in Table II it becomes evident that the percentage uncertainty in the values obtained for the *relative* areas is considerably smaller than estimated above to prevail for *absolute* areas. For example the ratio of the surface area of catalyst 954 to catalyst 973-I obtained by comparing the relative volumes of a particular gas adsorbed at point B on the isotherms for the catalysts is 22.8 as judged by the carbon monoxide isotherms: 23.3, from the isotherm for nitrogen at −195.8° and 22 for that at −183°; 22 from argon at −183° and 22.7 from butane at 0°. The maximum deviation from the mean of these values is less than 5%. The closeness of agreement is easily understood if one bears in mind that the absolute density of packing of one gas compared to another is of no concern in this calculation; it is merely necessary that a given gas have the same density of packing on one catalyst as on another in order to obtain good agreement among the relative surface areas calculated from the isotherms of different gases. It may also be noted that for the six iron catalysts studied it makes little difference whether the comparison of the relative adsorption volume is made for point A, B, or E. In the above comparison for example the ratio of the surfaces as judged from the −195.8° nitrogen isotherm is 23.3 for point B, 21.3 for point E and 23.6 for point A. Isotherms of the type included in the present paper should therefore prove very useful for obtaining comparatively accurate relative surface areas of various catalysts.

The purpose of this paper is not to present a discussion of all of the detailed characteristics of the shape of the low temperature isotherms but to show wherein they hold the key to a useful method for measuring the absolute and relative surface areas of catalytic substances. Nevertheless it may be of interest to call attention to several as yet unexplained peculiarities of the higher pressure portion of the physical isotherms on the unpromoted iron catalyst 973. The nitrogen isotherms at −195.8° for this catalyst differ from those on all the other catalysts by exhibiting a decrease in slope at a pressure higher than that corresponding to the linear portion of the isotherm. The phenomenon is apparently real and reproducible since the nitrogen isotherms on both samples of this catalyst invariably have this peculiar "break." Furthermore, the argon isotherm on this catalyst is unusual in that the higher pressure portion of the curve constitutes a second linear portion rather than a curve convex to the pressure axis. Elucidation of these peculiarities and of other detailed characteristics of the low temperature isotherms must await experimental data on a larger variety of finely divided materials and the completion of an attempt now being made to develop a theory capable of accounting for the shape of the isotherms throughout their entire pressure range.

Summary

Adsorption isotherms of some or all of the following gases have been determined on six different iron synthetic ammonia catalysts at the temperatures indicated: nitrogen and argon at −195.8°; nitrogen, argon, carbon monoxide and oxygen at −183°; methane and nitric oxide at −140°; nitrous oxide and carbon dioxide at −78°; ammonia at −36°; and *n*-butane at 0°. These

isotherms together with data for the chemisorption of carbon monoxide on the catalysts at −183 and −78° and for the activated adsorption of hydrogen appear to afford a means for measuring the absolute as well as the relative surface areas of the iron catalysts. Evidence is also presented to show that the aluminum oxide promoters tend to concentrate on the surfaces of the iron synthetic ammonia catalysts, 1 and 10% Al_2O_3 in the sample as a whole resulting in the covering of about 35 and 55% of the surface, respectively.

WASHINGTON, D. C. RECEIVED MAY 10, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of 1,4-Dimethyl-6,7-methylenedioxyphenanthrene and of Certain Substituted 9,10-Dimethyl-1,2,5,6-dibenzanthracenes

BY RUSSELL BLISS AKIN[1] AND MARSTON TAYLOR BOGERT

Following up our recent work[2] on the synthesis of 1,4-dimethylphenanthrene by the Pschorr process, we have carried out a similar series of reactions using 6-nitropiperonal in place of *o*-nitrobenzaldehyde, and have thus obtained the corresponding methylenedioxy derivative (II) of the dimethylphenanthrene. Further, by substituting the 2,5-dimethyl-*p*-phenylenediacetic acid for the 2,5-dimethylphenylacetic acid, the analogous 1,2,5,6-dibenzanthracene derivatives (IV and VI) have been prepared.

Experiments are now under way for the hydrolysis of these methylene ethers to the corresponding di- and tetrahydroxy compounds. Preliminary tests with anhydrous aluminum bromide have shown that this is not a satisfactory reagent for the purpose, and the attack is being continued by different methods.

One of the compounds (VI) described in the present paper is being tested by the Crocker Institute of Cancer Research, because of the well-known cancerigenic potency of 1,2,5,6-dibenzanthracene itself.

As our experimental work must now be interrupted for several months, it seems desirable to report here the results secured to date, and to add that these were obtained many months before the appearance of the recent paper by Fieser, Hershberg, Long and Newman,[3] on the hydroxy derivatives of 3,4-benzpyrene and 1,2-benzanthracene; and those of Hill and Short[4] on 1-methoxy-2-methyl; of Higginbottom, Hill and Short[5] on 4-methoxy-1-methyl; and of Hill, Short, Stromberg and Wiles,[6] on 3-methoxy-1-methyl phenanthrenes. In view of these publications from Harvard and from the Manchester College of Technology, we are continuing our own work mainly in the direction of the 1,2,5,6-dibenzanthracene derivatives.

Analyses.—The analytical work recorded in the Experimental Part was carried out by Dr. Donald Price and Mr. Saul Gottlieb.

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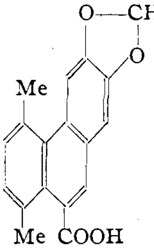
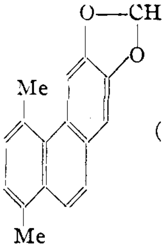


(I)



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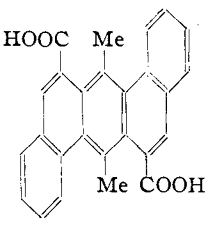

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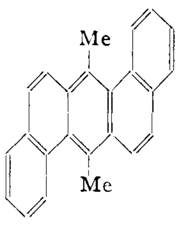

(IV)

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[1] Ferguson Fellow, Columbia University, 1934–35 and 1936–37.

[2] Akin, Stamatoff and Bogert, THIS JOURNAL, **59**, 1268 (1937).

[3] Fieser, Hershberg, Long and Newman, THIS JOURNAL, **59**, 475 (1937).

[4] Hill and Short, *J. Chem. Soc.*, 260 (1937).

[5] Higginbottom, Hill and Short, *ibid.*, 263 (1937).

[6] Hill, Short, Stromberg and Wiles, *ibid.*, 510 (1937).