tion into standard acid and titration of the excess acid. The solubility curve is shown plotted in Fig. 2, together with the values reported by Gerasimov[5] and the determination of Schreinemakers at 30°. The present values fall on a straight line up to 60°, with only a slight falling off above that temperature.

Summary

1. The aqueous solubility of magnesium chromate has been determined from 0 to 75°; the saturating phases in this temperature range are $MgCrO_4 \cdot 7H_2O$ and $MgCrO_4 \cdot 5H_2O$. Two other hydrates, $MgCrO_4 \cdot 2H_2O$ and $MgCrO_4 \cdot H_2O$, also have been detected, in the thermal decomposition of the pentahydrate in air. Anhydrous magnesium chromate can be prepared by complete dehydration.

2. The aqueous solubility of $(NH_4)_2CrO_4$ has been determined from 0 to 75°.

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[CONTRIBUTION FROM MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Heats of Adsorption of Gases on Iron Synthetic Ammonia Catalysts at Low Temperatures[1]

BY RALPH A. BEEBE AND NELSON P. STEVENS

Emmett and Brunauer[1a] have developed a method for measuring surface areas of adsorbent materials based on the analysis of the low temperature van der Waals adsorption isotherms of gases near their boiling points. For any given adsorbent, the values for the surface area calculated from the van der Waals isotherms of different gases are generally in good agreement. When the method was applied to several iron catalysts[2] the apparent areas were anomalously high for certain gases such as carbon monoxide and carbon dioxide as compared with nitrogen and argon. This discrepancy was attributed to the presence of chemisorbed oxides of carbon in addition to a van der Waals adsorbed monolayer. By determining the amount of adsorption in excess of that necessary to fill the van der Waals monolayer, it was possible to estimate the quantity of chemisorbed gas present. The chemisorbed volume was also estimated from the volume of gas which, once adsorbed, could not be removed at a temperature considerably above the adsorption temperature. These data were used as a basis for certain important conclusions concerning the preferential concentration of alkali in the surface of alkali promoted iron catalysts.

Although the above method of estimating the fraction of chemisorption appeared to be justifiable, it seemed desirable to obtain an independent experimental check on the method. In a number of investigations in this Laboratory the heats of adsorption have been used in differentiating between van der Waals adsorption and chemisorption. Therefore, at Dr. Emmett's suggestion, we have measured the heats of adsorption in the temperature region of 0 to −183° for several gases on two iron catalysts, one doubly promoted and the other unpromoted. In anticipation, it may be said that our results substantiate in general the conclusions of Emmett and Brunauer as regards the magnitude of the chemisorption processes on these surfaces.

Experimental

Apparatus.—The general apparatus assembly in the present measurements has been described in earlier publications.[3,4] The calorimeter is shown in Fig. 1 of the paper by Beebe and Orfield. In the final experiments on the iron catalysts (Series B on 931 and 973), the calorimeter was modified slightly to permit sending a continuous stream of hydrogen through the catalyst mass during the period of activation. This modification involved the substitution of a metal tube without perforations in the place of the perforated tube D shown in Fig. 1 (Beebe and Orfield). This tube was seated at the lower end in such a way that the incoming hydrogen passed down through the tube D and then up through the catalyst and out through a side tube (not shown in the figure) at the top of the glass mantle. This outlet tube was closed by a glass tap during the adsorption measurements.

In the final experiments with catalyst 931, the assembled calorimeter contained the following materials: platinum calorimeter and cover 34.09 g., platinum side tube 1.14 g., copper tube and vertical vanes 42.45 g., copper shot 14.61 g., iron-nickel tubes 3.65 g., iron catalyst (unreduced oxide)[5]

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[1] Supported by a grant from the Penrose Fund of the American Philosophical Society.

[1a] Brunauer and Emmett, THIS JOURNAL, **59**, 2682 (1937).

[2] (a) Emmett and Brunauer, *ibid.*, **59**, 310 (1937); (b) **59**, 1553 (1937); (c) **62**, 1732 (1940).

[3] Beebe and Orfield, *ibid.*, **59**, 1627 (1937).

[4] Beebe and Dowden, *ibid.*, **60**, 2912 (1938).

[5] All catalyst weights given in this paper are those of the unreduced oxides.

21.04 g. The heat capacity of the calorimeter at each of the three temperatures, 0, −78, and −183°, was calculated from the known specific heats of the materials comprising it.[5] A similar calorimeter made with a silver cylinder was used with catalyst 973.

As in the previous measurements, the temperature changes were recorded by means of a single junction copper-constantan thermocouple and sensitive galvanometer, the deflection of which was photographically recorded. The galvanometer sensitivity was calibrated by sending through it a suitable small current (approximately 10^{-9} ampere) obtained by delivering a potentiometrically measured low voltage through a known high resistance. Knowing the current sensitivity of the galvanometer and the resistance of the thermocouple circuit (all copper leads to avoid local thermal e. m. f.) it was possible to read temperature changes directly from the galvanometer deflections.

As might have been expected the calorimetric conditions were most satisfactory at −183°, the relatively high rate of heat loss at 0 and −78° introducing a factor which led to some uncertainty in estimating the true temperature rise due to adsorption. Moreover, the bath temperature at −78°, using carbon dioxide snow and alcohol, was much more variable than that of the ice–water-bath or the liquid oxygen. However, by using a heavy copper shield surrounding the glass mantle of the calorimeter to integrate minor variations in temperature it was found that reasonably satisfactory heat measurements could be obtained even at −78°. The data obtained at −78 and 0° may in certain unfavorable instances[6] be in error by 10 or 12%, but even these approximate data are of value because the discussion of these results is based on order of magnitude rather than exact values.

Materials.—The two iron catalysts studied were obtained from the United States Department of Agriculture, Bureau of Agricultural Chemistry and Engineering, through the courtesy of Dr. P. H. Emmett. These were a promoted catalyst 931 containing 1.59% K_2O and 1.3% Al_2O_3 and an unpromoted catalyst 973 of "pure" iron containing 0.15% Al_2O_3 impurity. These iron catalysts have been used in the extensive surface area studies by Emmett and Brunauer already cited. These authors have shown that a long period of high temperature reduction in a rapid stream of pure, dry hydrogen is necessary to obtain maximum activity and adsorptive capacity, and that rather careful control of the rate of hydrogen flow and temperature of reduction is necessary to obtain reproducible results. In our preliminary experiments with each catalyst the design of the calorimeter vessel did not permit the streaming of hydrogen gas, and it was necessary to remove the water vapor produced during reduction by alternate addition and removal of the hydrogen gas at successively higher temperatures up to 475° with catalyst 931 and 400° with catalyst 973. This method produced surfaces less active than those obtained by Emmett and Brunauer. Hence it was decided to modify the calorimeter in the manner already described to permit the flow of gas through the catalysts.[7] Using a rate of 500 cc. of hydrogen per minute, and the following reduction schedule: four to five hours at 350°, twelve hours at 400°, forty-eight hours at 450°, twenty-four hours at 500°, the doubly promoted catalyst 931 acquired an adsorptive capacity which was in good agreement with that observed by Emmett and Brunauer. Catalyst 973 treated in the same way was found to be considerably less active than the preparation of these authors, probably as a result of sintering during the long reduction at high temperature.[8]

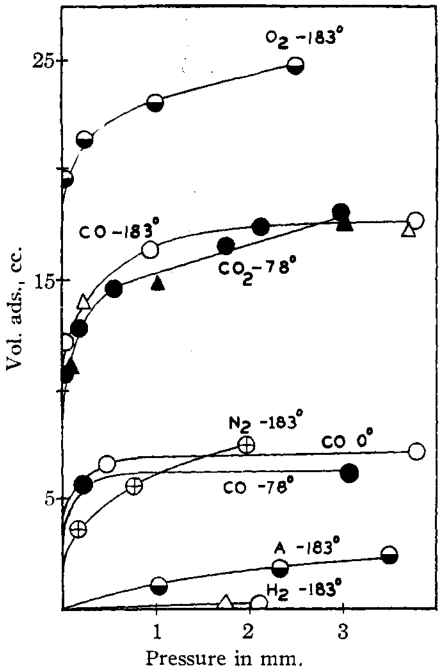

Fig. 1.—Adsorption isotherms on 21.04 g. of iron catalyst 931 (doubly promoted).

We shall refer to the measurements on the catalysts prepared by alternate addition and removal of hydrogen as Series A for each catalyst, and to the later measurements on the surfaces prepared by reducing in streaming hydrogen as Series B for each. In both Series A and B the surfaces were cleaned after each set of differential heat measure-

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[6] An exact estimate of the heats per mole of gas was especially difficult with the last increment measured for carbon dioxide at 0° and for carbon monoxide at 0 and −78°. In these cases, the rapid initial adsorption was followed by a slow disappearance of residual gas, and the time–temperature curves which in the absence of any slow adsorption process might have been expected to show a decrease of temperature with time, exhibited instead an increase. In the most extreme case the volume of carbon monoxide adsorbed at 0° (sixth increment, Fig. 2) was 0.56 cc. after three minutes but 0.85 cc. after twenty-three minutes. In this case the value 0.56 and the temperature rise after three minutes were used in calculating the heat per mole of gas. A similar procedure was followed with the other measurements at 0 and −78° although in most of the increments the additional volume adsorbed between three and twenty-three minutes was less than 6% of the total volume adsorbed, a value much less than in the extreme case cited above.

[7] In modifying the calorimeter as above described, it was necessary to sacrifice the advantage of the perforations in the inner tube D (Beebe and Orfield, Fig. 1) which formerly served to minimize the effect of "non-selective" adsorption.

[8] This failure to reproduce the activity observed by Emmett and Brunauer on catalyst 973 is not surprising, because this unpromoted surface appears to be much more sensitive than the promoted catalyst, such as 931, to minor differences in the method of reduction. This is shown in the data of the above authors on catalysts 973-I and 973-II.[2b]

ments by the high temperature treatment with hydrogen with final evacuation for one hour at the maximum temperature used in the reduction. In series B a twelve-hour treatment in streaming hydrogen at 500° preceded the final evacuation between sets.

The hydrogen used for activating the catalyst surface was purified by passing tank hydrogen over copper filings at 500°, then through Drierite and finally through a liquid-air trap containing copper wool, using an all-glass train. Pure hydrogen used for the adsorption measurements was purchased from the Air Reduction Sales Company, as were also the argon, helium and nitrogen.

The carbon monoxide, made by dropping 90% formic acid on concentrated sulfuric acid in an apparatus which was well evacuated before the generation of gas started, was purified by passing it through the following train: (1) Drierite, (2) solid potassium hydroxide, (3) a liquid-air trap, (4) copper filings at 525°, and (5) solid potassium hydroxide.

The oxygen was prepared by the method described previously.[4]

The carbon dioxide was prepared by heating solid sodium bicarbonate in a previously evacuated apparatus and removing water vapor by means of a Drierite tube and solid carbon dioxide trap.

Results[9]

Doubly Promoted Catalyst 931 (1.59% K_2O, 1.3% Al_2O_3).—The data shown in Table I are typical of the results obtained in the preliminary studies. Although 21.04 g. of catalyst was used, the volume adsorbed is given in the third column in cc. of gas per gram of catalyst. In the fourth column are given the differential heats, for successive small increments added, up to the point where the residual gas pressure was approximately 3 mm.

Table I

Heats of Adsorption on Catalyst 931 (Series A)

Gas adsorbed	Temp. of ads., °C.	Total vol. ads., cc./g.	Diff. heats of adsorption kcal./mole
CO	0	0.065[a]	23.1 19.7 16.9 19.0
CO	−183	.505	8.9 6.4 6.0 5.9 4.7 4.2
CO_2	−78	.446	27.7 26.4 22.9 14.1 11.6 11.2 9.3 8.9

[a] In comparison with the results of Emmett and Brunauer and with our own results in Series B in which a flow method of reduction of the catalyst surface was employed, the ratio of carbon monoxide adsorption at 0° to that at −183° is surprisingly low in Series A on both catalysts (see also Table III). This low ratio is difficult to explain although it seems obvious that it is the result of the incompleteness of the reduction by the static method employed in Series A.

The results of the final experiments (Series B) with catalyst 931 are presented in greater detail. The order of the experiments was: CO at −183°, H_2 −183°, A −183°, CO 0°, N_2 −183°, CO −78°, CO_2 −78°, CO −183°, CO_2 −78°, CO_2 0°, O_2 −183°. The isotherms are given in Fig. 1 and the heats in Figs. 2 and 3 and Table II. Except in the cases already discussed with carbon monoxide at −78 and 0° and carbon dioxide at 0°, there was little drift in the residual pressure with time, indicating the absence of slow adsorption. The points shown in Fig. 1 are based on volume and pressure data taken three minutes after the admission of a given increment.

Table II

Heats of Adsorption on 21.04 G. of Catalyst 931 (Series B)

Vol. of gas, cc. Admitted	Vol. of gas, cc. Adsorbed	Resid. press., mm. × 10^3	Galv. defl., mm.	Diff. heats of adsorption, kcal./mole	Total vol. ads., cc.
		CO_2 at −78°			
1.01	1.01	0[a]	86.0	31.8	1.01
1.10	1.10	0	82.0	27.7	2.11
1.09	1.09	0	72.0	24.5	3.21
1.68	1.68	0	108.5	23.8	4.89
1.67	1.67	0	95.8	21.3	6.56
1.71	1.71	0	77.0	16.7	8.27
1.01	1.01	5	32.0	11.8	9.28
1.43	1.43	36	43.0	11.2	10.71
1.99	1.96	166	49.5	9.5	12.66
1.99	1.91	562	44.4	8.6	14.57
2.17	1.91	1750	41.9	8.1	16.49
1.00	0.92	2140	18.7	7.6	17.40
0.75	.57	3000	12.0	7.9	17.97
		CO at −183°			
0.38	0.38	0[a]	15.5	16.8	0.38
.82	.82	0	27.0	13.5	1.21
2.17	2.17	0	57.0	10.9	3.39
2.21	2.21	1	43.0	8.1	5.60
2.17	2.16	54	26.0	5.0	7.75
2.23	2.21	86	26.5	5.0	9.97
4.02	3.98	254	43.0	4.5	13.94
3.93	2.93	3730	26.3	3.7	16.88

[a] It was impossible to measure pressures less than 1 × 10^{-3} mm. on the rather insensitive McLeod gage used in these measurements. Pressures designated as "0" might more properly be given as "less than 1 × 10^{-3} mm."

The satisfactory agreement between duplicate sets of measurements with both carbon monoxide at −183° and carbon dioxide at −78° is shown in the isotherms and in the heat data of Figs. 2 and 3. This indicates that the carefully controlled method of preparation was successful in giving the surface reproducible activity.

The differential heats with nitrogen and argon at −183° were, respectively, 4.4, 3.6, 3.3, 2.5 kcal., and 3.0, 2.6, 2.5 kcal. for successive increments, indicating pure van der Waals adsorption as might have been expected. These heats, obtained on a relatively bare surface, may be

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(9) We are indebted to Dr. D. A. Dowden for a large part of the preliminary measurements at −183° (Series A) on both catalysts.

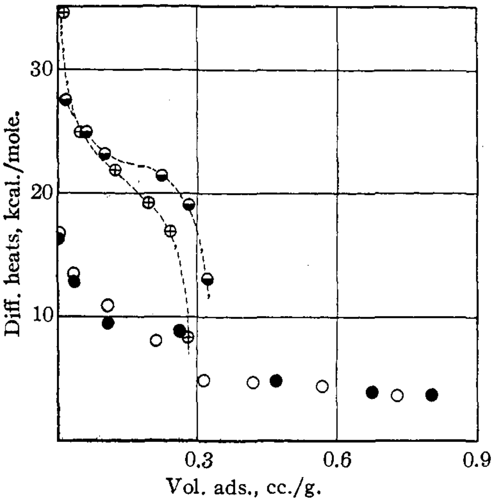

Fig. 2.—CO on catalyst 931 (Series B): 0° ◒; −78° ⊕; −183° Set 1 ●; Set 2 ○.

compared with values ranging from 2.7 to 1.6 kcal. calculated by Emmett and Brunauer from their isotherms on iron surfaces on which the adsorbed monolayer was nearing completion.[2b]

The hydrogen adsorption at −183° was very small for the low pressure range studied. A single increment of 0.38 cc. was adsorbed at 2 mm. residual pressure on the 21.04-g. sample of catalyst (weighed as unreduced oxide) giving a heat of 5.3 kcal. per mole. A check determination produced the same heat value a second time. It is noteworthy that this heat was of the same order of magnitude as those for hydrogen on chromic oxide gel at −183°.[4] For reasons discussed in the chromic oxide work, heats of the order of 5 kcal. for hydrogen are too high to be accounted for by van der Waals forces alone, and the observed adsorption of hydrogen on iron at −183° must therefore be, in part at least, a chemisorption process.

Pure Iron Catalyst 973.—Typical data obtained with catalyst 973 are presented in Table III. Gas increments were added, up to residual pressures of about 3 mm.

TABLE III

HEATS OF ADSORPTION ON CATALYST 973 (33.33 G.)

Gas adsorbed	Temp. of ads., °C.	Total vol. ads., cc./g.	Diff. heats of ads., kcal./g.
		Series A	
CO	0	0.015	Between 19 and 12[a]
CO	−183	.151	9.3 6.8 5.8 4.9 4.2
CO_2	−78	.051	8.7 6.5
		Series B	
CO	0	0.068	20.2 12.2
CO	−183	.082	12.1 6.4 4.2
CO_2	−78	.027	10.7 7.7

[a] Interpretation of time–temperature curve uncertain here.

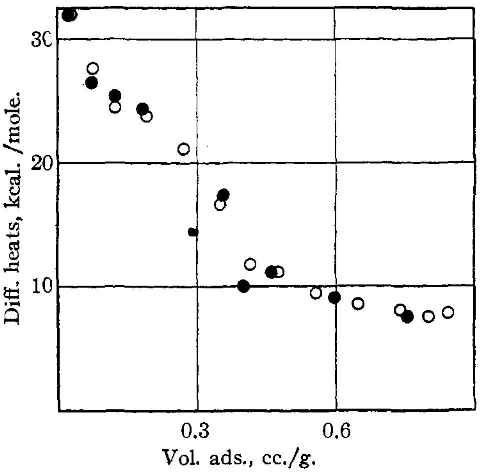

Fig. 3.—CO_2 at −78° on catalyst 931 (Series B): Set 1 ●; Set 2 ○.

Oxygen Experiments.—The results of the heat measurements with oxygen are given in Fig. 4, including three sets with catalyst 931 and one with 973. Only in Set III on catalyst 931 was the surface at maximum activity, this set being measured at the end of Series B on this catalyst. In Sets I and II on catalyst 931 the method of preparation of the surface before adsorption was as nearly identical as possible. In spite of the lack of completely satisfactory agreement among the data given in Fig. 4,[10] there can be no doubt of the order of magnitude of these data.

Emmett and Brunauer[2c] have found that the behavior of oxygen on iron catalysts at −183° is especially anomalous, the volume of oxygen chemisorbed being from five to ten times as great as the chemisorbed volume of carbon monoxide.[11] Since it is probable that the carbon monoxide completely covers the iron atoms in the surface with a chemisorbed layer at −183°, it seems necessary to assume that the oxygen must penetrate beneath the surface, attaching itself to several underlying layers of iron atoms.

Our results with oxygen substantiate those of

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(10) Unlike the other gases studied at −183°, oxygen produced heats that varied in a rather irregular fashion even within the same set. These variations may perhaps be due to the effects arising from non-selective adsorption not eliminated by the calorimeter used.[7] It would be expected that this difficulty would be especially important with the oxygen adsorption which is a very rapid and irreversible reaction. The time–temperature curves for the second half of Set III gave evidence of considerable variation in the bath temperature because the supply of liquid oxygen had run low at this point making it impossible to keep the calorimeter immersed to a suitable depth.

(11) Emmett and Brunauer found that the amount of oxygen taken up was strongly dependent on the manner in which the oxygen was passed into the catalyst chamber; if it was done rapidly the oxygen sorption was higher than if done slowly. As a result of this, exact checks are not to be expected in the ratio of oxygen to carbon monoxide chemisorbed.

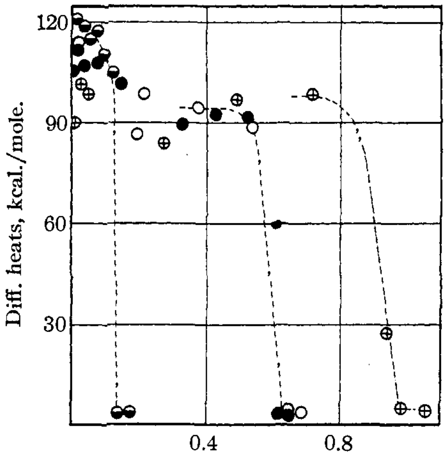

Fig. 4.—O_2 at −183°: catalyst 973 (Series A) ⊖; catalyst 931 (Series A), Set I ●; Set II ○; (Series B) Set III ⊕.

Emmett and Brunauer. For instance, in Set III on catalyst 931, it is obvious that the nature of the binding forces changes abruptly from a strong chemical type to the van der Waals type at about 0.9 cc. of oxygen taken up per gram of catalyst since this is the point of abrupt change from heats of the order of 80–100 kcal. down to 4 kcal. If this is compared with the 0.20 cc. estimated for the carbon monoxide chemisorption on the same catalyst surface, we obtain a ratio of 4.5 for oxygen to carbon monoxide. Furthermore, the heats observed for the chemisorption process approach in magnitude the heats of formation of the oxides of iron,[12] indicating that the nature of the process here is not unlike oxide formation.

Although all the oxygen increments up to 0.9 cc./g. (Set III, catalyst 931) were adsorbed instantaneously without leaving any measurable residual pressure, the observed evolution of heat was not all instantaneous. After an initial relatively low rise in temperature, a considerable amount of heat was more slowly evolved over a period of twenty minutes or more indicating that some highly exothermic process was occurring after the initial disappearance of the oxygen from the gas phase. This phenomenon has been observed previously by Beebe and Dowden working with carbon monoxide, nitrogen, and oxygen at −183° on chromium oxide,[4] and has been interpreted by these authors as evidence that the gases initially adsorbed in the van der Waals state have undergone a slow change into the chemisorbed state. A similar interpretation seems justifiable in the present case dealing with oxygen on an iron surface. The persistence of this highly exothermic reaction long after the admission of the oxygen and its virtual disappearance from the gas phase, rules out the possibility that the excessively large oxygen pick-up might be due to a sudden heating of the catalyst resulting from the first small amount of oxygen admitted.[2b]

Discussion

The heat of van der Waals adsorption of carbon monoxide may be expected to fall within the range from 3 to 5 kcal. and certainly would not exceed 8 kcal.; with the more easily condensable carbon dioxide the range of van der Waals heats would probably be 7 to 10 kcal., certainly not exceeding 12 kcal. With these facts in mind it is apparent that our measurements indicate the presence of chemisorption of carbon monoxide on both catalysts and of carbon dioxide on catalyst 931 only.

Our data on catalyst 931 (Series B) appear to be in quantitative agreement with those of Emmett and Brunauer. It is impossible to compare total surface areas because our measurements were not carried out to sufficiently high pressures to effect the completion of the monolayer of adsorbed gas. On the other hand, a comparison of the volumes of *chemisorbed* gas is possible. Emmett and Brunauer[2c] found in their most recent measurements on catalyst 931 that the volumes of *carbon monoxide* chemisorbed per gram of catalyst at −78° were 0.248, 0.233 and 0.220 cc. in three successive experiments, and that 0.218 and 0.198 cc. per g. were adsorbed in two successive experiments at −183°, the slight reduction in adsorptive capacity being attributed to a gradual sintering of the catalyst even at a reduction temperature not exceeding 500°. Figure 2 shows that the differential heat values at −78° change abruptly from the chemisorption to the van der Waals range in the vicinity of 0.25 cc. per g. At −183° this change is not so abrupt, but it is reasonable to assume that heats above 8 kcal. represent chemisorption, making 0.20 cc. per g. a plausible point for the transition from chemisorption to the van der Waals type. The higher amount of chemisorption of carbon monoxide at 0° is qualitatively

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[12] The heats evolved in the formation from the elements of FeO, Fe_2O_3 and Fe_3O_4 are, respectively, 128, 127, and 133 kcal. per mole of oxygen.

consistent with the findings of Emmett and Brunauer although they give no quantitative data for this temperature. These authors found that the chemisorption of *carbon dioxide* at −78° on catalyst 931 ranged as high as 0.36 cc. per g., a value which is in very good agreement with the region of transition from heats of chemisorption to those of van der Waals adsorption as shown in Fig. 3, the heats being 30–16 kcal. up to 0.39 cc. per g. and dropping rather abruptly to 12–8 kcal. beyond that point.

The adsorption measurements on catalyst 973, although not so reproducible as with 931, have considerable significance in comparison with the results obtained with 931. The absence of any initial high heats with carbon dioxide on catalyst 973 at −78° appears to substantiate Emmett and Brunauer's conclusion that the adsorption of this gas is almost exclusively of the van der Waals type here.[13] On the other hand, with carbon monoxide at −183°, the initial heats of 9.3 and 12.1 kcal. on 973 in Series A and B, respectively, as well as the high values at 0° appear to indicate the presence of chemisorption of carbon monoxide on this catalyst as postulated by Emmett and Brunauer.[14]

The experimental evidence of Emmett and Brunauer indicates chemisorption of carbon monoxide on both the doubly promoted catalyst 931 and the pure iron catalyst 973, but indicates also the virtual absence of chemisorbed carbon dioxide on 973, as well as on another catalyst 954 singly promoted by alumina although carbon dioxide is chemisorbed on the alkali promoted catalyst 931. To explain these observations, these authors make the reasonable assumption that the carbon dioxide is chemisorbed exclusively on the potassium oxide in the surface but that the chemisorption of carbon monoxide occurs on the surface iron atoms. Now, in the case of catalyst 931, by comparing the area covered by chemisorbed carbon dioxide with the total area determined from the van der Waals adsorption isotherms of nitrogen, the important conclusion is reached that the potassium oxide promoter, although comprising only 1.59% of the catalyst, must cover approximately 75% of its surface.[2a] It is significant that our heat measurements provide independent evidence for the correctness of the experimental data on which the above conclusions are based.

It is noteworthy that the heats of chemisorption of carbon monoxide are almost identical in value at 0 and −78° but considerably less at −183° (see Fig. 2). This appears to indicate that there is a great change in the nature of the binding between −183° and −78° but very little further change if the temperature is raised to 0°. There is evidence that iron carbonyl is formed at 0 or −78°.[2c] If one takes the binding energy of the Fe–CO bond in iron pentacarbonyl as 12 kcal. and the heat of vaporization of iron as 91 kcal. ("I. C. Tables") then the heat of formation of $Fe(CO)_5$ from carbon monoxide with the iron still attached to the lattice would be 151 kcal. or about 30 kcal. per Fe–CO bond. This value is in qualitative agreement with the observed heat of adsorption at −78° and at 0°, especially for the initial increments admitted to a reduced surface.

Summary

1. The differential heats of adsorption of a number of gases have been measured in the temperature region 0 to −183° using a doubly promoted iron catalyst and a pure iron catalyst, both previously studied as to adsorption by Emmett and Brunauer.

2. The heat measurements indicate that the adsorption of nitrogen and of argon at −183° is exclusively of the van der Waals type; that the adsorption of hydrogen at −183°, and of carbon monoxide at −183, −78 and 0° is in part chemisorption; and that carbon dioxide is chemisorbed on the alkali promoted catalyst at −78°, although the adsorption of this gas on the pure iron catalyst is exclusively van der Waals.

3. The conclusions listed above are in general in agreement with those of Emmett and Brunauer based on an analysis of the low temperature isotherms.

4. The heat evolved in the irreversible adsorp-

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(13) Emmett and Brunauer did find slight chemisorption of carbon dioxide even on the pure iron catalyst, which they attributed to the possible presence of alkali impurities.[2a] The value 10.7 kcal. found by us on 973 at −78° (see Table III) may conceivably be evidence for slight chemisorption of carbon dioxide; however, this evidence is far from conclusive in view of the fact that Lamb and Ohl [THIS JOURNAL, **57**, 2154 (1935)] found heats as high as 12.4 kcal. for the van der Waals adsorption of carbon dioxide on chabazite.

(14) Attention should be called to the fact that the heats of the carbon monoxide adsorption on the pure iron catalyst are smaller than on the doubly promoted catalyst; 973 has values up to 12 kcal. at −183° and up to approximately 19 at 0°, 931 has values up to 16 kcal. at −183° and 29 at 0°. Dr. Brunauer (private communication) points out that this difference is probably due to sintering of the iron surface of the unpromoted catalyst, and furthermore states that he has noticed in his experiments that not only does the quantity of the carbon monoxide chemisorption decrease if the iron surface is strongly sintered but also the binding of the adsorbed gas to the iron becomes weaker. This is evidenced by the fact that it is possible to pump off a part of the chemisorbed carbon monoxide at −78° from a strongly sintered iron catalyst.

tion of oxygen at −183° approaches, in order of magnitude, that of iron oxide formation; and the form of the time–temperature curves with oxygen at −183° indicates that the adsorption process involved is complex. A similar complex process was previously observed with chromic oxide gel at −183°.

RECEIVED MAY 24, 1940

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Reactions Relating to Carbohydrates and Polysaccharides. LXII. The Relation between Concentration and Viscosity of Polyoxyethylene Glycols

BY EDWIN L. LOVELL[1] AND HAROLD HIBBERT

In a recent communication, Fordyce and Hibbert[2] have described the relation between the degree of polymerization of polyoxyethylene glycols $HO(CH_2CH_2O)_xH$ and their solution viscosities at basic-molar concentration (4.4%) in two solvents (dioxane and carbon tetrachloride). They found that their data could be accurately represented by the Staudinger equation written in the form $\eta_{sp}/c_{bm} = K'_m(M) + \beta$, where β is a small constant. However, the Staudinger equation, although invariably written in terms of the reduced viscosity η_{sp}/c_{bm}, is apparently not meant to imply that the specific viscosity is a linear function of the concentration over any appreciable range of concentrations, as Staudinger has used[3] the early empirical equation of Arrhenius[4]—$\ln \eta_r = Kc$ —(where K is a constant) for both polyethylene oxides and polystyrenes. This is also the equation used by Kraemer[5] for the extrapolation of viscosity results to zero concentration in calculating the "intrinsic viscosity," an important quantity for characterizing high-polymer solutions. However, the question of the concentration effect of viscosity for such solutions has been the subject of controversy for many years, and a wide variety of empirical equations has been suggested.[6] In a recent investigation by Daneš,[7] carried out with carefully fractionated polystyrenes, it is shown that neither the Arrhenius nor the Staudinger equation is capable of describing the experimental results. No alternative is suggested. Inasmuch as Daneš' investigation was carried out under much more carefully-controlled conditions than used by Staudinger, especially with regard to the use of uniform products, considerable doubt is thrown on the validity of either of these equations. A similar investigation has therefore been carried out with a number of synthetic, chain-uniform polyoxyethylene glycols. Furthermore, some synthetic mixtures of these substances have been prepared, and their viscosities compared with theory.

Experimental

The synthesis and proof of chain-uniformity of the polyoxyethylene glycols and the dichloride used in the experiments have been reported elsewhere.[8] 1,4-Dioxane was purified according to the recent method of Hess.[9] Carbon tetrachloride was fractionated and redistilled from solid potassium hydroxide.

The solutions were prepared as follows. The pure, dry solute (about 0.5–2 g.) was weighed into a 10-ml. volumetric flask (previously standardized with water) and dissolved by adding solvent to a point just below the volume mark. When a uniform solution finally resulted, the total volume was adjusted accurately to the mark by adding a further small portion of solvent (less than one drop). These operations were carried out in a thermostat. Finally, the total weight of the solution was measured.

During use, each solution was stored in a desiccator containing an open dish filled with the anhydrous solvent. This was found to be completely effective in preventing evaporation. Other precautions were taken to avoid evaporation during the subsequent operations.

Mixtures were prepared by weighing the solutions directly into a weighing bottle (again with suitable precautions) and measuring the resulting density.

The viscometer was the same instrument as used by Fordyce and Hibbert.[2] A thermostat maintained the temperature constant to within ±0.02°. In calculating the viscosities, the solution densities were taken into account. A summary of the experimental data appears in Table I.

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[1] Holder of a Studentship of the National Research Council of Canada, 1939–1940.

[2] Fordyce and Hibbert, THIS JOURNAL, **61**, 1912 (1939).

[3] Staudinger, "Der Aufbau der hochmolekularen Verbindungen," Verlag von Julius Springer, Berlin, 1932.

[4] Arrhenius, *Z. physik. Chem.*, **1**, 287 (1887).

[5] Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

[6] Many of these have been reviewed critically by Hess and Philippoff, *Ber.*, **70B**, 639 (1937); see also Meyer and Wolff, *Kolloid-Z.*, **89**, 194 (1939).

[7] Daneš, *Kolloid-Z.*, **68**, 110 (1934).

[8] Fordyce, Lovell and Hibbert, THIS JOURNAL, **61**, 1905 (1939); Fordyce and Hibbert, *ibid.*, **61**, 1910 (1939).

[9] Hess, *Ber.*, **71B**, 262 (1939).