[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Heats of Adsorption at −183°. Carbon Monoxide on Copper

BY RALPH A. BEEBE, GEORGE W. LOW, JR., AND SEYMORE GOLDWASSER

Recent investigation[1] has shown that the reaction $H_2 + D_2 = 2HD$ is catalyzed by chromium oxide and supported nickel at temperatures as low as −183°, giving evidence for an activated as well as a van der Waals adsorption even at this low temperature. Because in general the magnitude of the heat effect is approximately one order higher for activated adsorption than for van der Waals, experimental data on heats of adsorption have been considered important in deciding which type is predominant in any given case. However, Gould, Bleakney and Taylor,[1] by indirect reasoning from their results on the catalytic activity of chromium oxide at low temperatures, have suggested that the heat of activated adsorption of hydrogen on this catalyst is very small at −183° and therefore of the magnitude commonly believed to attend van der Waals adsorption. For a more complete understanding of the phenomena at −183° it is apparent that experimental data on the heats of adsorption are needed. These are often calculated by application of the Clapeyron–Clausius equation to pressure data at two temperatures; however, this procedure cannot be used if the residual pressure is too small to measure as is often the case especially for the initial portions of the surface covered. The authors have therefore considered it important to develop a direct calorimetric method for measuring the heat values at low temperatures.

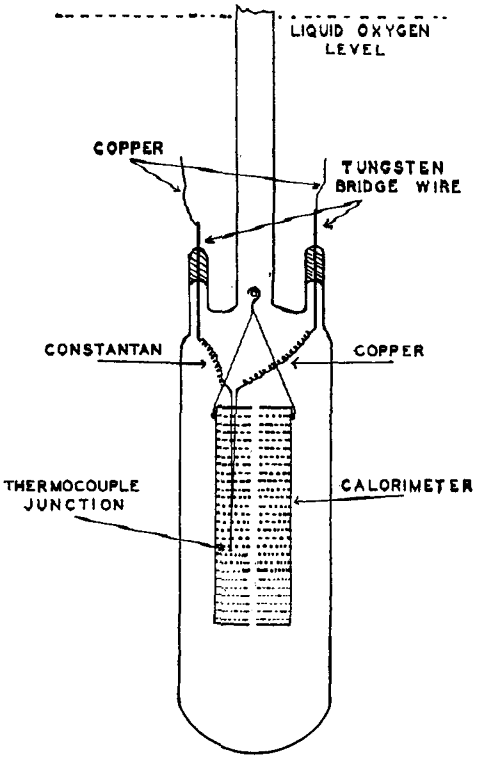

Fig. 1.

Because the problems attendant upon the heat measurements at 0° have been studied carefully by one of us[2] for carbon monoxide on copper, this case has been chosen as a point of attack in developing a method at −183°.

Experimental

Apparatus.—The apparatus was identical with that of Beebe and Wildner[2b] except for the method of leading in the thermocouple wires. In one method (Fig. 1) tungsten wire bridges were substituted for the "Picein" seals which had been satisfactory at 0° but would not hold the vacuum at −183°. Because it seemed reasonable to question the reliability of results for which the tungsten bridge wires were used, a second method (Fig. 2) was also employed. In this method, the copper–constantan thermo-junction, inserted at the point A, was pushed to the bottom of the platinum finger F, which was closed at its lower end. The platinum finger fitted loosely into a thin-walled copper sleeve which was embedded in the catalyst, the loose fit being necessary to facilitate the assembly of the apparatus. A reference junction not shown in Fig. 2 was inserted into the heavy copper jacket mentioned below. This calorimeter had the advantage that the gases never came in contact with the thermoelement. Both calorimeters contained the copper adsorbent granules in layers separated by copper gauze disks to improve the conditions for heat distribution.[2b] A heavy copper jacket

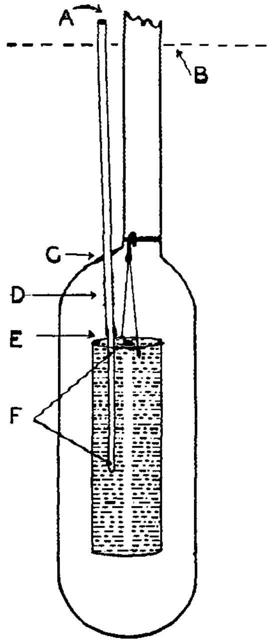

Fig. 2.—B, liquid oxygen level; C, ring seal; D, Pyrex to soft glass seal; E, soft glass to platinum seal.

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[1] Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

[2] (a) Beebe, *Trans. Faraday Soc.*, **28**, 761 (1932); (b) Beebe and Wildner, THIS JOURNAL, **56**, 642 (1934).

1.1 cm. thick, suspended in the liquid oxygen bath and fitting closely around the Pyrex calorimeter chamber, served to integrate local variations in the bath temperature. The liquid oxygen[3] was contained in a large Dewar flask of 4.5 liters capacity. This large volume of liquid was essential to maintain sufficient constancy and uniformity of bath temperature.

The sensitivity of the single junction copper-constantan thermoelement was of course much less at −183° than at 0°; but this unfavorable factor was partially compensated because of the lower heat capacity of copper at the lower temperature. In the case of cylinder 1, for instance, the water equivalent was 3.93 as compared to 6.59 calories at 0°. The galvanometer deflection was 1 mm. per 0.0069° at a distance of one meter. The voltage sensitivity of the thermocouple in the region of −183° was calibrated against a secondary standard copper-constantan couple kindly provided by Professor Evald Skau of Trinity College, Hartford, Conn.

Materials.—In all, four different calorimeter cylinders filled with copper granules were used. Cylinder 1 with its charge of copper had been used for the measurements at 0° reported by Beebe and Wildner.[2b] This active copper, designated as copper 1, had been exposed to the atmosphere for some time, and after again reducing with hydrogen it had lost about 30% of its activity at the time of the previous measurements. At no time had the adsorbent been removed from the cylinder. On this as well as on all the other copper samples used, the rate of adsorption at −183° was practically instantaneous. Copper 2, used in cylinders 2 and 3, came from the same original batch as copper 1 but had been sealed in glass for nearly three years. Its adsorptive capacity was approximately the same as that of copper 1. Copper 4 used in cylinder 4 was prepared at the time of these experiments by reduction of copper oxide granules in hydrogen, first at 120°, and finally at 170°; its adsorptive capacity was about half that of copper 1. Cylinders 1 and 2 were used in method 1 (Fig. 1), and cylinders 3 and 4 in method 2 (Fig. 2). Because all the cylinders had the same dimensions, their weight when assembled varied little from that of cylinder 1 which was 71.5 g., of which 40.0 g. was due to active copper adsorbent.

Procedure.—Before each series of measurements the catalyst was outgassed for five hours at 170°. To hasten the establishment of thermal equilibrium between the calorimeter and its surroundings a small pressure of pure helium was admitted to the calorimeter which was then allowed to stand overnight in the liquid oxygen bath. In experiments by method 1, this helium was pumped out before the first increment of carbon monoxide was admitted, but with method 2 it was necessary to leave a small helium pressure (0.02 mm.) in the calorimeter vessel at the start of a series; otherwise the rate of transfer of heat from the active copper mass to the platinum finger containing the thermocouple was too slow to produce satisfactory time-temperature curves. In method 1 the uninsulated copper wire of the thermocouple was crowded against the copper gauze cylinders of the calorimeter probably in several places making much better thermal contact between the calorimeter and the thermocouple than the loosely fitting platinum finger of method 2. As in the previous work[2b] the time-temperature curves were photographically recorded.

Discussion of the Method

Previous experiments[2a] have demonstrated that two factors, (a) slow conduction of heat and (b) non-uniform adsorption, are unfavorable to satisfactory conditions for the heats of adsorption measurements; and the efficiency of our calorimeter in minimizing the effects of these factors at 0° has been discussed.[2b] Compared to 0°, effective heat transfer is favored at −183° by the greater thermal conductivity of copper at that low temperature; but this favorable factor is offset by the much lower rate of heat transfer by radiation and by the residual gases in the calorimeter. Judging from the similarity in form between the time-temperature curves obtained at the two temperatures, it would seem that the factors favorable and opposed to good heat distribution just about balanced each other. For the initial stages of adsorption at 0°, it was shown by experiment that the process was non-uniform, *i. e.*, adsorption occurred on those successive layers of adsorbent with which the carbon monoxide first came into contact.[2a] Although not demonstrated experimentally, it is probable that the same phenomenon is present at −183°. The calorimeter is designed to minimize, but does not completely eliminate, this effect with the result that the differential heats for the initial increments measured and reported below, are probably lower than the true differential heats for reasons previously given.[2b]

The time-temperature curves obtained by method 1 (Fig. 1) were similar to those at 0°, having the form of curves I, II and III in Fig. 2 of the paper by Beebe and Wildner,[2b] for initial, intermediate, and final increments of carbon monoxide added to the surface. Using method 2, all the time-temperature curves had the form of curve III mentioned above, the more rapid rise to a maximum and the subsequent more rapid cooling being due to the presence of the helium gas (0.02 mm.). Unlike those at 0°, these curves at −183° contained irregularities which were probably due to lack of complete uniformity in temperature of the liquid oxygen bath. The amplitude of these variations varied from 0.5 mm.

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(3) This liquid oxygen guaranteed 99% pure was purchased from the Air Reduction Sales Company. Because of the high degree of purity of the oxygen and because a relatively small percentage of it was evaporated, no change in its boiling point was noticeable during the measurements.

in most of the curves to 2 mm. in the worst cases. It is roughly estimated that they introduced random errors of 5 to 10% in reading the temperature changes from the curves.

Results

Three series of differential heats were measured for cylinder 1, and two each for cylinders 2, 3 and 4, making nine series in all. The results for the four series on copper 2 are shown in Fig. 3 in which the total heat evolved is plotted against cc. of carbon monoxide adsorbed. The total heat

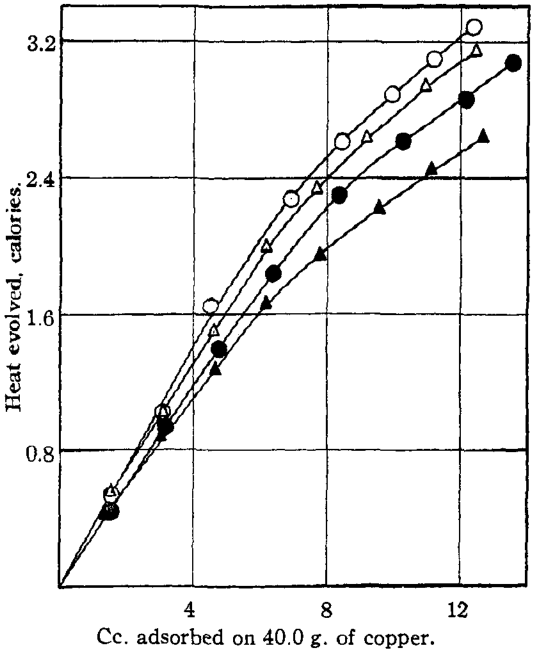

Fig. 3.—○, Cylinder 2, series 1; △, cylinder 2, series 2; ●, cylinder 3, series 1; ▲, cylinder 3, series 2.

was calculated by summation of the measured heats for separate successive increments of gas. It is important to observe that method 1 (Fig. 1) was used in the measurements on cylinder 2, but that method 2 (Fig. 2) was used for cylinder 3; however, copper 2 was used in both cylinders. The fair concordance of the data obtained by the two methods is evidence for the reliability of both methods of measurement. The failure of the results for the four series to check more closely than they do is probably due to the lack of complete similarity of the copper surfaces used in the two cylinders, although they came originally from the same batch of copper, and also to the lack of complete reproducibility of these surfaces in successive series. In Table I is given a comparison of the volumes adsorbed at the arbitrarily chosen pressure of 0.8 mm. This table does not of course give any information concerning the relative percentages of active points in the surfaces used. In Table II are shown more complete details of two typical series. After the completion of series 2, cylinder 1 (Table II), the copper was outgassed for two hours at −183°. The increments a, b and c, then added, yielded low differential heats of the order of 3 kcal. per mole. Measurements on copper 4 which had lower adsorptive capacity than the others gave the following differential heats for successive increments: 7.3, 5.5, 4.9, 3.8, 4.0 kcal. per mole.

TABLE I

Cylinder no.	Series no.	Cc. adsorbed
2	1	12.40
2	2	12.20
3	1	13.45
3	2	11.80

TABLE II

	Volume of gas Admitted	Volume of gas Adsorbed	Resid. press. mm. $\times 10^3$	Galv. defl., mm.	Diff. heat of adsorp., kcal./mol.	Total vol. ads. cc.
			Cylinder 1, Series 2			
1	1.32	1.32	0	22.3	8.7	1.32
2	1.44	1.44	0	25.6	8.9	2.75
3	1.34	1.34	0	17.2	6.5	4.10
4	1.40	1.40	0	16.2	5.9	5.51
5	1.28	1.28	16	10.0	4.0	6.79
6	1.40	1.37	43	10.7	4.0	8.16
7	1.34	1.26	158	9.7	3.9	9.42
8	1.37	1.20	395	7.8	3.3	10.62
9	1.46	1.16	836	8.0	3.5	11.78
	Outgassed to		27			
a	1.52	1.46	103	9.9	3.3	9.3
b	1.40	1.25	331	7.9	3.2	10.6
c	1.40	1.12	751	7.1	3.3	11.7
			Cylinder 3, Series 1			
1	1.57	1.57	0	23.0	7.0	1.57
2	1.58	1.58	0	22.5	6.8	3.15
3	1.58	1.58	0	20.0	6.1	4.73
4	1.62	1.62	0	20.5	6.1	6.35
5	2.02	2.00	1	21.5	5.1	8.35
6	1.98	1.91	99	15.0	3.7	10.26
7	2.16	1.86	450	11.6	3.0	12.13
8	1.97	1.44	1050	10.1	3.4	13.56

Discussion

In all our measurements for carbon monoxide on copper at −183° the differential heats for the first few cc. of gas added to the surface have been of the order of 8 kcal. which, although less than the values at 0°,[2b,4] is several times greater than the heat of vaporization of carbon monoxide. It

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(4) Measurements of differential heats at 0° on copper 1 and copper 2 using the tungsten bridge calorimeter (Fig. 1), confirmed the previous work of Beebe and Wildner which showed that the heats were of the order of 19 to 14 kcal. per mole.

therefore seems probable that the adsorption is a combination of activated and van der Waals adsorption favoring the former for initial stages but changing in ratio progressively to the latter as successive increments of gas are added to the surface. This is in agreement with the conclusion of Benton and White[5] based upon indirect experimental evidence.

The technique worked out in detail for carbon monoxide on copper should be applicable to other gas–solid combinations at −183°. For reasons given in the introduction, direct experimental measurements of heats of adsorption are needed at low temperatures on chromium oxide. The technique described above is now being applied to the latter adsorbent.

Our thanks are due to the Committee on Grants-in-Aid of the National Research Council for supplying funds for technical assistance in this work.

Summary

1. A method has been described for the direct measurement of the differential heats of adsorption of carbon monoxide on copper at −183°.

2. The differential heats are of the order of 8 kcal. per mole in the initial stages, and decrease to 3 kcal. in the later stages of the adsorption.

3. The results seem to indicate that a considerable part of the adsorption for the initial increments of gas is of the activated type even at the low temperature of −183°.

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[5] Benton and White, This Journal, **54**, 1385 (1932).

[Contribution from the Chemical Laboratory, University of Illinois]

X-Ray Diffraction Studies of Built Up Films[1]

By G. L. Clark and P. W. Leppla

The development by Langmuir and Blodgett[2] of a technique for the preparation of foliated films of any desired number of molecular layers permits for the first time the study of x-ray diffraction effects produced by a known number of planes. Clark, Sterrett and Leppla[3] reported distinct diffraction patterns from nine or more layers of stearates prepared by Blodgett's method. Langmuir and Schaefer[4] have since shown by chemical analysis of the unimolecular layer skimmed from solutions containing calcium or barium ions that the built up films vary continuously in composition from pure acid at *p*H 2 to pure soap at *p*H 11. In view of the fact that the soaps and the acids crystallize in different systems, and since, furthermore, several modifications of the fatty acids are known, the structure of the composite built up films was investigated by diffraction methods.

Experimental.—Films were prepared of stearates of lead, calcium and barium by means of a motor-driven device to ensure freedom from vibration and the highest possible perfection of the individual layers. To eliminate the necessity for oscillating the specimen in the path of the x-ray beam, curved surfaces were used as originally proposed by Trillat.[5] For the measurement of the long spacing, *d*, a radius of 15 mm. was employed. To each order corrections were applied for the actual position of the origin of the diffracted spot. To increase the intensity of the pattern for the study of films of only a few layers, the radius was increased to a maximum of 50 cm. Copper Kα radiation was used.

A double lining of lacquer overlaid with paraffin was used in the brass trough to prevent contamination of the solutions with copper ions. For the measurement of *p*H an antimony electrode was employed.

Since films do not adhere to glass at low *p*H, lacquered surfaces were used in the acid range. Molecules adhere to glass or metal by their polar groups and exist in an odd number of layers. On lacquer the hydrocarbon end of the chain is attached to the surface and the films exist in an even number of layers.

Composition of the Surface Film.—Unimolecular stearate films were skimmed from the surface of dilute calcium, barium and lead salt solutions at varying hydrogen-ion concentrations, the material air-dried, packed into tiny cells and transmission diffraction patterns registered. Side spacings characteristic of both the acid and the soap appeared in each case, the intensities indicating complete agreement with Langmuir and Schaefer's[4] conclusions.

Structure of the Built Up Films.—From the mechanism of the transfer process the gross structure readily may be inferred to be the alternating

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[1] From a thesis presented by P. W. Leppla to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1936. Presented before the 91st meeting of the American Chemical Society, Kansas City, Mo., April, 1936.

[2] Blodgett, This Journal, **57**, 1007 (1935).

[3] Clark, Sterrett and Leppla, *ibid.*, **57**, 330 (1935).

[4] Langmuir and Schaefer, *ibid.*, **58**, 284 (1936).

[5] Trillat, *J. phys. radium*, [6] **10**, 32 (1929).