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

Heats of Adsorption at −183°: Hydrogen on Chromic Oxide

BY RALPH A. BEEBE AND HORACE M. ORFIELD

In a recent publication,[1] a technique was described for measuring heats of adsorption at −183° and results were reported for carbon monoxide on copper. Moreover, it was shown that heat measurements for the case of hydrogen on chromic oxide should be especially interesting. Using an improved technique, these measurements have been made and the results are now presented.

Experimental

Apparatus.—Except for the calorimeter itself, the apparatus was identical with that used by Beebe, Low and Goldwasser.[1] As in the former work, the temperature change was measured by a single junction copper–constantan thermocouple and sensitive galvanometer, and the time–temperature curves were recorded photographically.

The improved form of the calorimeter, shown in Fig. 1, had the advantage over previous models that the space between the silver cylinder which contained the chromic oxide, and the outer Pyrex tube, could be highly evacuated even for later increments of hydrogen when there was a residual gas pressure over the chromic oxide. This ensured a slow loss of heat from the calorimeter to its surroundings. After the completion of each successive differential heat measurement, a low pressure of helium in this outer space served to bring the temperature of the calorimeter rapidly back to that of the surrounding bath.

The thermocouple wires were led in either by inserting directly to the bottom of the metal tube E which was soldered to the outside of the silver cylinder, or by means of the tungsten bridge wires F and F′, the thermojunction itself being soldered to the cylinder in the latter case. Both these methods gave satisfactory results. Some difficulty was experienced in obtaining the necessary glass to metal tube seals which would withstand the rather rigorous treatment of heating in hydrogen to 400° to activate the chromic oxide, and subsequent cooling to −183° for the actual heat measurements. The requirements were met, however, by a special iron–nickel alloy suggested by Dr. A. W. Hull of the Research Laboratories of the General Electric Company. The silver cylinder containing the adsorbent was hard soldered to the iron–nickel tube which was then sealed to a special soft glass; the latter was attached to Pyrex by means of a graded seal.

The inner metal tube D, which was perforated with many small holes, served to bring the incoming hydrogen into simultaneous contact with a relatively large part of the chromic oxide surface, thereby minimizing the effect of "non-uniform" adsorption.[2-4]

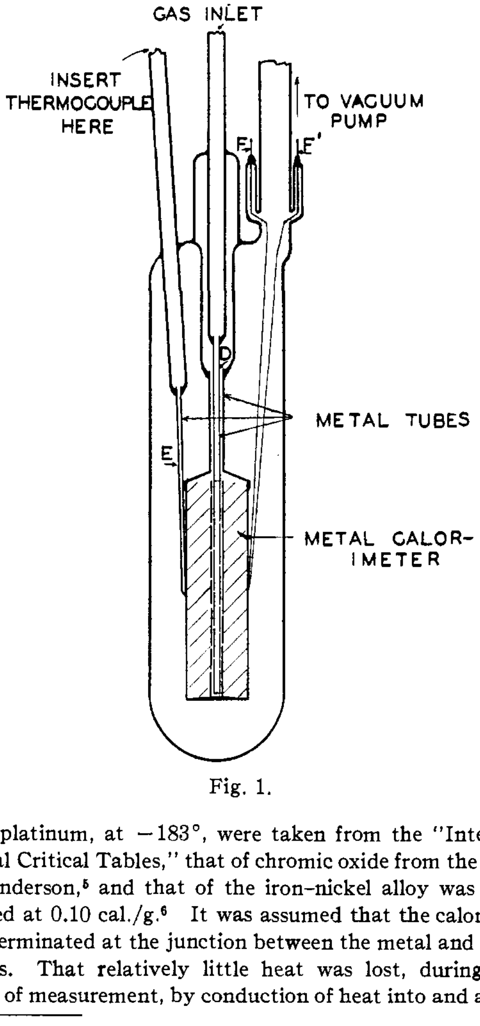

Fig. 1.

Rapid heat distribution was ensured by using an all metal calorimeter. Six vertical vanes of perforated copper foil (not shown in Fig. 1) were inserted inside the silver cylinder; moreover, fine copper shot was intermixed with the chromic oxide granules. One assembled calorimeter contained the following materials: silver cylinder and cover 36.54 g., copper foil 16.60 g., copper shot 34.16 g., platinum tube D 0.95 g., iron–nickel tube 3.6 g., chromic oxide adsorbent 11.95 g. The heat capacity of the calorimeter was calculated from the weights and specific heats of the materials comprising it. The specific heats of copper, silver and platinum, at −183°, were taken from the "International Critical Tables," that of chromic oxide from the data of Anderson,[5] and that of the iron–nickel alloy was estimated at 0.10 cal./g.[6] It was assumed that the calorimeter terminated at the junction between the metal and glass tubes. That relatively little heat was lost, during the time of measurement, by conduction of heat into and along

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[1] Beebe, Low and Goldwasser, THIS JOURNAL, **58**, 2196 (1936).

[2] Beebe and Wildner, *ibid.*, **56**, 642 (1934).

[3] That the adsorption of the initial increments of hydrogen on chromic oxide at −183° was "non-uniform," was demonstrated by a separate experiment using a procedure similar to that described by Beebe for the case of carbon monoxide on copper at 0° (Ref. 4).

[4] Beebe, *Trans. Faraday Soc.*, **28**, 761 (1932).

[5] C. Travis Anderson, THIS JOURNAL, **59**, 488 (1937).

[6] The authors are aware that the chromic oxide used by Anderson had been heated to high temperature to drive off residual water, while that used in the adsorption experiments was of necessity never taken above 400°, and contained approximately 2.5% of water. Neglect of this factor, however, together with the possible error in estimating the heat capacity of the iron–nickel alloy could not have introduced an error in excess of 4% in calculation of the total heat capacity of the calorimeter.

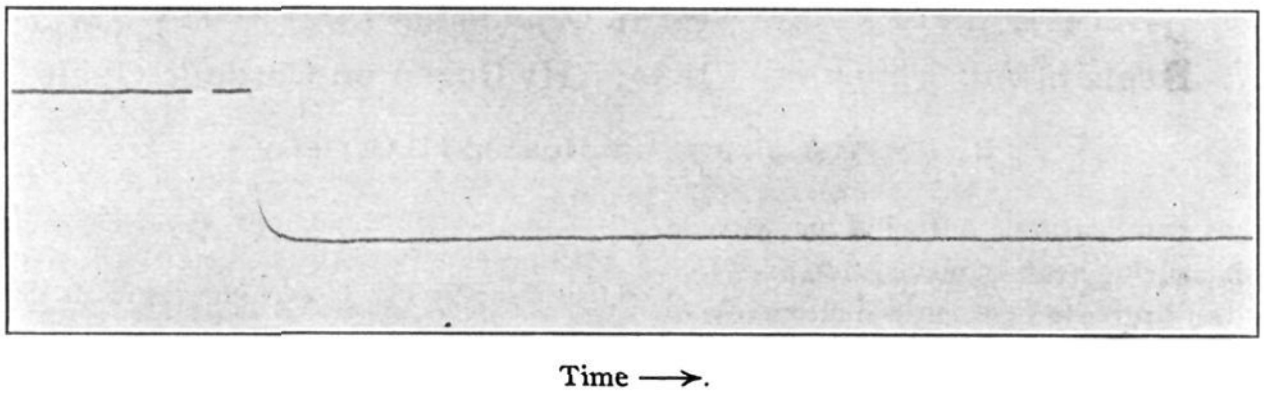

Fig. 2.

the glass tubes, was shown by the very slow rate of decrease of temperature after adsorption (see Fig. 2).

A few measurements were made with a liquid oxygen calorimeter essentially the same as that described by Dewar,[7] the heat being measured by the volume of oxygen gas evaporated from the liquid in which the adsorption tube was immersed.

Materials.—The chromic oxide was made as described by Burwell and Taylor[8] for their sample No. 9. The temperature of reduction was never allowed to exceed 400°, thus avoiding the "glow" phenomenon and resultant deactivation of the adsorbent. Before each series of heat measurements the chromic oxide was heated in hydrogen for one to two hours at 400° and was then outgassed at that temperature for fourteen to sixteen hours. This preparation adsorbed 3 cc. of hydrogen per gram of adsorbent at 1 mm. pressure and −183°; adsorption was complete in less than two minutes.

Discussion of the Method

The form of the time–temperature curves obtained indicates that the calorimeter shown in Fig. 2 is the most satisfactory yet employed in this Laboratory. In Fig. 2 is given a reproduction of a typical twenty-minute curve which was originally recorded photographically. Curves of this type were obtained for all stages of the adsorption whether for initial or for final increments. The rapid rise to maximum temperature and subsequent maintenance of that temperature indicate almost ideal calorimetric conditions. As a result, the authors believe that the data obtained are very reliable. However, it must be recognized that the effect of "non-uniform" adsorption, although minimized, probably has not been eliminated completely. As was the case in previous work, this would mean that the differential heats for initial increments are probably lower than the true differential heats.[2]

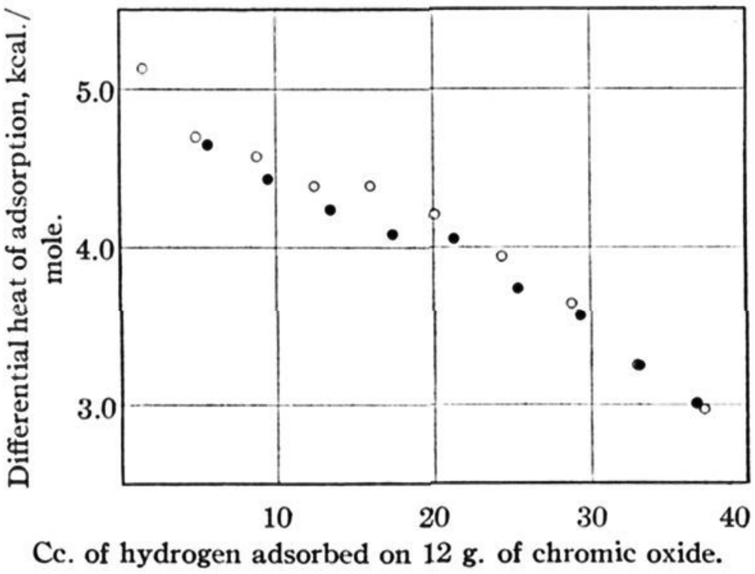

Fig. 3.—○, series A; ●, series B.

Results

The results for two satisfactory series (A and B) are shown in Fig. 3; and greater detail for series A is given in Table I.[9] These measurements were made with the calorimeter shown in Fig. 1 with the tungsten lead wires for the thermocouple. It was found that the portion

TABLE I

SERIES A

	Volume of gas		Resid. press., mm. × 10^3	Galv. defl., mm.	Diff. heat of adsorp. kcal./mole	Total vol. ads., cc.
	Admitted, cc.	Adsorbed, cc.				
1	3.06	3.06	0	39.5	5.13	3.06
2	3.69	3.69	0	43.5	4.69	6.75
3	4.01	4.01	0	46.0	4.57	10.76
4	3.41	3.41	0	37.5	4.39	14.17
5	3.67	3.67	27	40.5	4.39	17.85
6	4.51	4.51	37	47.5	4.20	22.36
7	4.05	4.05	71	40.0	3.94	26.41
8	4.58	4.54	242	41.5	3.64	30.95
9	4.54	4.36	978	35.5	3.25	35.31
10	4.24	3.81	2722	28.5	2.97	39.12

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(7) Dewar, *Proc. Roy. Soc.* (London), **74**, 122 (1904).

(8) Burwell and Taylor, THIS JOURNAL, **58**, 697 (1936).

(9) Several series of measurements were made prior to the two here reported but, in many of these, trouble with leaks in the metal to glass seals resulted in partial deactivation of the catalyst. With this less active chromic oxide, the differential heats for initial increments were about 4 kcal.; the heats for later portions, however, checked those given in Table I for corresponding residual gas pressures. In a typical series of this sort, the amount adsorbed was 60% of that taken up in the absence of leaks, and the heat values were successively, 4.1, 3.7, 3.7, 3.6, 3.6, 3.4, 3.3, 3.0 kcal. These results indicate that the most active parts of the surface had lost their adsorptive capacity probably by admission of small amounts of air.

of the hydrogen which was adsorbed with a measurable residual gas pressure, was easily removed from the surface by outgassing at −183°. The heat values then obtained on admission of hydrogen to the partially degassed surface were of the order of 4.0 to 3.0 kcal.

It was hoped that it would be possible to confirm the above results by the entirely different calorimetric method of Dewar.[7] Although the results obtained by the two independent methods did agree in order of magnitude, it was found that the data obtained by the Dewar method were not consistent, and that the values found seemed to depend upon the size of the hydrogen increment adsorbed. For instance, for 20 cc. of hydrogen added to an active chromic oxide surface, the apparent differential heat value was 5.4 kcal. per mole; but for two successive increments of 10 cc. each on the same surface after degassing, the values were, respectively, 4.7 and 3.4 kcal. It seems probable that the cause of this discrepancy lay in superheating effects in the liquid oxygen. The discordance in the above data casts some doubt upon the quantitative value of Dewar's heats of adsorption measurements on charcoal, although the order of magnitude of his results is doubtless correct.

Discussion

Gould, Bleakney and Taylor[10] have shown that the reaction $H_2 + D_2 \rightleftarrows 2HD$ is catalyzed by chromic oxide at −183°, and that equilibrium can be approached from either side in the presence of this catalyst. From these observations it must be concluded that the adsorption of hydrogen is, in part at least, of the activated type, and further that desorption of hydrogen from that part of the surface which is catalytically active, must proceed at an appreciable rate which would of necessity result in a relatively low activation energy of desorption especially at the low temperature under consideration. Now the activation energy of desorption is equal to the sum of the activation energy of adsorption plus the heat of adsorption. It therefore follows that the heat of activated adsorption of hydrogen at −183° must be small on some part, at least, of the chromic oxide surface.

It seems probable that the part of the surface which best satisfies the conditions favorable to catalytic activity would be that portion studied by us on which the adsorption was reversible and the differential heats were 4.0 to 3.0 kcal. Here we have a reversible adsorption with a heat of relatively low value and yet higher than is commonly ascribed to van der Waals adsorption of hydrogen at this low temperature.[11] For the most active parts of the surface, the heats are apparently too high to permit rapid desorption, with the result that the adsorption process is irreversible. Moreover, it is probable that adsorption, at greater equilibrium hydrogen pressures than those studied by us, would change progressively to the van der Waals type as the surface became more completely covered. It would appear, then, that that part of the surface which possesses medium activity in the adsorption of hydrogen is the part which is most active in catalyzing the hydrogen–deuterium reaction.

It is important to obtain more data on heats of adsorption by direct measurement, especially because there is considerable doubt concerning the validity of heats calculated from the isosteres. This doubt arises because such calculations are based on the assumption that when equal amounts of gas are adsorbed at two different temperatures, the same part of the surface is covered. This assumption is often not a valid one.[12] The improved calorimetric technique will therefore be applied to several gas–solid adsorption systems at −183°.

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. An improved calorimetric method has been applied to the direct measurement of the differential heats of adsorption of hydrogen on chromic oxide at −183°.

2. The differential heats are of the order of 5 kcal. for the initial stages, and decrease to 3 kcal. in the later stages measured.

3. It is believed that the part of the surface, for which the heat of adsorption is in the vicinity of 4 to 3 kcal., is most probably the seat of catalytic activity in the reaction between hydrogen and deuterium.

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

[11] Taylor and Sickman [THIS JOURNAL, **54**, 602 (1932)] found a heat value of 1.1 kcal. for the van der Waals adsorption of hydrogen on zinc oxide in the low temperature range, and the heat for hydrogen on charcoal obtained by Dewar[7] by direct measurement at −183° was 1.5 kcal.

[12] Howard and Taylor, THIS JOURNAL, **56**, 2263 (1934).