2. This is the result which would be anticipated if the reaction proceeded by the usual mechanism for displacement reactions.

CHICAGO, ILLINOIS

The Sorption of Carbon Monoxide by Metals. Temperature Variation Experiments

BY CARROLL W. GRIFFIN

Introduction

The identification of two types of adsorption, namely, physical and activated, has been definitely established for gases on many solids. The existence of a third sorptive force has long been suspected and that this might be solution was mentioned by the author in the case of hydrogen and massive copper.[1] Further evidence to support this belief was obtained in studies of the sorption of hydrogen on supported copper,[2] on massive nickel,[3] on supported nickel,[4] and particularly by the "experiments with temperature variation."[5] In the last two studies the attack has consisted of bringing the gas into sorptive equilibrium with the metal at $-78.5°$, raising the temperature to $0°$ and, after measuring the equilibrium conditions, returning the temperature to $-78.5°$. In this manner it was revealed that the sorption at $-78.5°$ is followed first by a rapid desorption at $0°$ and then by a slower process (solution) at $0°$. Upon cooling again to $-78.5°$ the sorption is found to be greater than the original sorption at this temperature to an extent equal to the volume slowly taken up at $0°$.

The success of this method of study of course depends upon selecting two temperatures, one at which the secondary sorptive force, thought to be solution, is absent or is at a minimum, and the other at which it manifests itself distinctly. The amount of solution, and not simply its rate, will be greater at the higher temperature and also at higher pressures. These facts hold for the studies already cited.

It is obvious that -78.5 and $0°$ might not always be the temperature at which the two sorptive forces would distinguish themselves best. Thus, although Benton and White do not specifically so label the experiment immediately under their Table IV,[6] this is really a run "with temperature variation," the variation here being from 110 to 210°. In connection with their study of carbon monoxide on massive copper it might be emphasized that the authors did not find, after noting the desorption coming with the elevated temperature, any resorption (solution) as evidenced by a drop in pressure. Yet, when the temperature was again brought to 110°, the sorption of carbon monoxide amounted to 15.00 ml. as compared with an original 14.43 ml. It therefore seems, in the writer's opinion, since 0.57 ml. is more than ten times their experimental error, that actually solution of over half a milliliter did take place at 210°, in excess of any dissolved at 110°, but it occurred simultaneously with the desorption of the activated carbon monoxide molecules and *was overshadowed by the desorption*. For as long as both processes are taking place and the rate of desorption exceeds the rate of solution there can be no observable evidence of the latter, save the greater total sorption when return is made to the lower temperature. Only when the desorption at the higher temperature is completed quickly or is relatively small may one observe the pressure reversal which indicates that solution is taking place.

Sorption studies with temperature variation have been confined to hydrogen on metals with the exception that Benton and White have shown the general behavior of carbon monoxide on massive copper. Therefore, the present work was undertaken to learn whether or not the effects observed with hydrogen are common also to other gases. Platinum and copper were the metals selected and, since little or no solution can be expected with supported metals, both forms have been employed with platinum. With copper only the supported metal was used. Since it has already been shown that solution of carbon monoxide in massive copper becomes appreciable only above 0°, the temperatures selected for the supported copper

(1) Griffin, THIS JOURNAL, **49**, 2136 (1927).

(2) Griffin, *ibid.*, **57**, 1206 (1935).

(3) White and Benton, *J. Phys. Chem.*, **35**, 1784 (1931).

(4) Griffin, THIS JOURNAL, **61**, 270 (1939).

(5) Benton and White, *ibid.*, **54**, 1373 (1932); Griffin, *ibid.*, **63**, 2957 (1941).

(6) Benton and White, *ibid.*, **54**, 1373 (1932).

were 0 and 100°. Those for the two platinum sorbents were −78.5 and 0°, for von Hemptinne[7] found that a marked increase in the sorption of carbon monoxide on platinum takes place around −40°.

Experimental

The apparatus[8] and general method of making the runs[9] and the purification of carbon monoxide[1] have been described. The supported copper sample was the same as in a previous study.[2] The platinum samples also had been used before and their preparation reported.[10] Since it is not possible completely to remove adsorbed carbon monoxide from platinum surfaces by simple evacuation, its removal was accomplished by burning off with oxygen at 250° between runs. The oxygen was then washed off with hydrogen and the latter removed by pumping off at 250°. As usual, helium was employed as a reference gas.

Results

On each of the three sorbents a run was first made to measure the sorption at the lower temperature (0° for copper; −78.5° for platinum) at several pressures up to one atmosphere. Then a run was made at the higher temperature (100° for copper; 0° for platinum). After this three runs were made on each sorbent with temperature variation, using progressively greater volumes of carbon monoxide. The results are summarized in the tables and figures. Table I lists the data obtained with supported copper, and Tables II

TABLE I

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF CARBON MONOXIDE BY SUPPORTED COPPER (10.2 G. CU ON 40 G. OF BRICK)

(1) Gas taken up at 0°	Press.	88.4	362.2	512.9
	Vol.	3.00	3.55	3.63
(2) Initial value after warming to 100°	Press.	159.9	522.5	739.9
	Vol.	1.88	2.78	2.99
(3) Total sorption at 100° at pressures given in (2)		1.98	2.94	3.15
(4) Differences of (2) and (3)		0.10	0.16	0.16
(5) Final values reached at 100°	Press.	158.0	518.7	736.1
	Vol.	1.94	2.91	3.10
(6) After cooling to 0°	Press.	86.5	351.8	509.2
	Vol.	3.09	3.69	3.79
(7) Direct values at 0° at pressures given in (6)		2.98	3.54	3.63
(8) Differences of (6) and (7)		0.11	0.15	0.16

(7) von Hemptinne, Z. physik. Chem., **27**, 429 (1898).

(8) Pease, THIS JOURNAL, **45**, 1196 (1923).

(9) Benton and White, ibid., **54**, 1379 (1932).

(10) Griffin, ibid., **63**, 2957 (1941).

and III give the results for the platinum sorbents. The values in Row (2) of the tables represent the adsorption at the higher temperature for a given experiment (plus solution, if any, at the lower temperature). The differences given in Row (4) are the volumes of carbon monoxide dissolved at the higher temperature and at pressures of Row (2), while the differences given in Row (8) are the volumes dissolved at the higher temperature at pressures of Row (5). The sums of adsorption and solution are found in Rows (3) and (5).[9]

TABLE II

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF CARBON MONOXIDE BY 5 G. OF MASSIVE PLATINUM

(1) Gas taken up at −78.5°	Press.	15.1	249.5	462.6
	Vol.	3.97	4.58	4.59
(2) Initial values after warming to 0°	Press.	45.1	398.1	696.8
	Vol.	3.44	3.50	3.52
(3) Total sorption at 0° at pressures given in (2)		3.79	4.16	4.22
(4) Differences of (2) and (3)		0.35	0.66	0.70
(5) Final values reached at 0°	Press.	34.5	371.4	666.5
	Vol.	3.68	4.10	4.20
(6) After cooling to −78.5°	Press.	8.5	233.6	440.1
	Vol.	4.18	5.22	5.30
(7) Direct values at −78.5° at pressures given in (6)		3.86	4.58	4.61
(8) Differences of (6) and (7)		0.32	0.64	0.69

TABLE III

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF CARBON MONOXIDE BY SUPPORTED PLATINUM (3.9 G. PT ON 10 G. OF BRICK)

(1) Gas taken up at −78.5°	Press.	32.8	286.1	426.2
	Vol.	1.03	1.25	1.27
(2) Initial values after warming to 0°	Press.	51.4	400.6	592.4
	Vol.	0.82	0.97	0.99
(3) Total sorption at 0° at pressures given in (2)		0.85	1.02	1.06
(4) Differences of (2) and (3)		0.03	0.05	0.07
(5) Final values reached at 0°	Press.	49.8	399.0	590.2
	Vol.	0.87	1.02	1.06
(6) After cooling to −78.5°	Press.	32.4	284.6	424.4
	Vol.	1.05	1.32	1.35
(7) Direct values at −78.5° at pressures given in (6)		1.03	1.26	1.28
(8) Differences of (6) and (7)		0.02	0.06	0.07

The data of the three tables are brought together in the figures. Curve 3 in all the figures, giving the adsorption at the higher temperature, is obtained by subtracting the amount of dissolved carbon monoxide at a given pressure from the total sorption at that pressure as found from Curve 2.

As in the case of hydrogen[10] the extent of solution of carbon monoxide in supported metals is
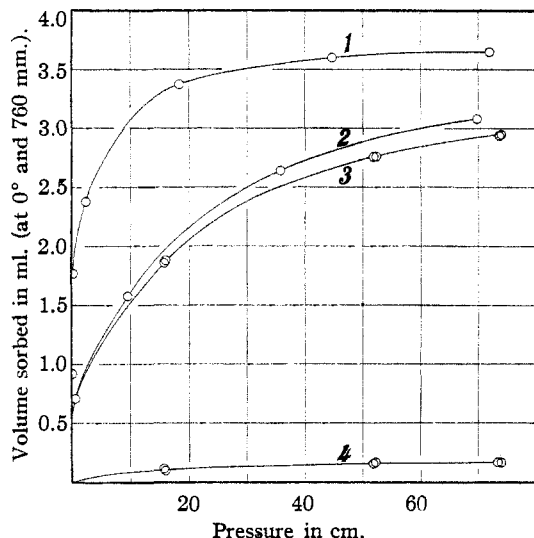
Fig. 1.—Sorption of carbon monoxide on supported copper, four moles of copper per 1000 g. of brick: curve 1, total sorption at 0°; 2, total sorption at 100°; 3, adsorption at 100°; 4, solution at 100°.

distinctly less than in massive metals. Thus, for carbon monoxide in platinum at 500 mm. pressure, the solution process accounts for 17% of the total 0° sorption for the massive form, and for only 5% for the supported form. For supported copper at 100° the figure is 5% both at 500 mm. and at 300 mm. pressure, whereas Benton and White found that for massive copper at 300 mm. pressure over 50% of the 100° sorption is due to solution.[11] The 17% solution for massive platinum is the smallest percentage yet found for a massive metal as may be seen from Table V of an earlier study.[10] Nevertheless, the present evidence substantiates the conclusion that when the sorbent is spread largely as surface the solution factor is much reduced.

The rate of sorption was rapid at low pressures for all three sorbents and somewhat slower at atmospheric pressure. The rate was about the same for massive as for supported platinum; this, as well as the rather unexpectedly low 17% solution for massive platinum, is believed due to the probability that there was a much greater amount of surface metal in this sorbent than is found in massive metals reduced from oxides in wire form. At atmospheric pressure two hours sufficed for equilibrium. This differs from the case of massive copper at 110° or higher under which conditions several days may not bring about equilibrium.

The rate of desorption of carbon monoxide on

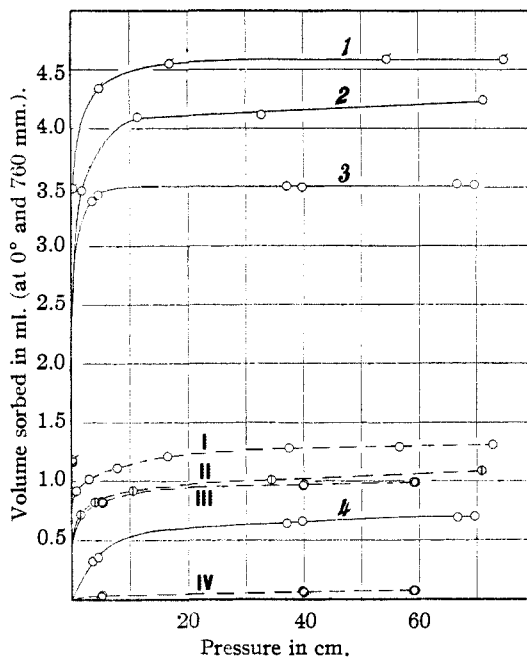(11) Benton and White, THIS JOURNAL, 54, 1373 (1932), see Fig. 7.

Fig. 2.—Sorption of carbon monoxide on platinum. Solid curves indicate massive platinum; broken curves indicate supported platinum, two moles of platinum per 1000 g. of brick: curves 1 and I, total sorption at −78.5°; 2 and II, total sorption at 0°; 3 and III, adsorption at 0°; 4 and IV, solution at 0°.

the two platinum sorbents when the temperature is elevated from −78.5 to 0° was slower than for hydrogen on platinum. As a result, the "initial sorption after warming to 0°," which is computed from the maximum pressure shown when the temperature is increased to 0°, (and which for hydrogen on platinum is almost immediate) was effected in about three or four minutes. Had the total desorption been immediate it follows that the "Initial values after warming to 0°" as shown in Row (2) of these tables would have been slightly higher for the observed pressures and thus somewhat lower for the calculated volumes. In turn this would mean that the values of Row (4), representing solution, would be rather greater. Because of these considerations the values in Row (8) for a given series of experiments should be more trustworthy than those of Row (4), and the fact that good checks have been obtained in Rows (4) and (8) (note that the pressures corresponding to the volumes for the two rows differ somewhat) indicates that in these particular experiments the maximum pressures of Row (2) did not materially differ from the actual values, had the latter been obtainable, which prevailed before the solution process had attained a finite value.

Summary

Measurements with temperature variation have been made for the sorption of carbon monoxide on supported copper and on massive and supported platinum. The results are qualitatively similar to like measurements of hydrogen on massive and supported metals and show that the presence of a secondary sorptive force is probably a general characteristic of metallic sorbents.

This factor, apparently solution, manifests itself only to a small extent with supported sorbents where the metal is largely exposed as surface. With massive metals and carbon monoxide the secondary action is over three times as great in the case of platinum, and about ten times as great in the case of copper, when compared with their respective supported forms.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Chemical Separation of the Isotopes of Hydrogen by the Addition of Metals and Compounds of Metals to Water, Acids and Bases. I. Relative Efficiencies of Specific Reactions. The Effects of Certain Factors other than Temperature[1]

BY HERRICK L. JOHNSTON AND CLYDE O. DAVIS

The possibility of obtaining separation of isotopes of hydrogen by displacement reactions of metals with acids was suggested by Washburn and Urey.[2] The first experimental results on displacement reactions were reported independently by L. and A. Farkas[3] and by ourselves.[4] Horiuti and Szabo[5] confirmed our own value of 2.5 for the separation coefficient in the Na–H₂O reaction, in experiments in which they introduced water vapor onto metallic sodium. More extensive observations at 90° have been reported by Hughes, Ingold and Wilson,[6] whose data differ somewhat from our own. Recently, Reyerson, Johnson and Bemmels[7] have reported qualitative data on the isotope separation which results when calcium carbide is treated with water.

The present paper describes quantitative investigations of the reactions of lithium, sodium, potassium, calcium, calcium carbide and aluminum carbide with water; magnesium, granulated and mossy zinc, c. p. and commercial iron, manga-

nese, aluminum and ferrous sulfide with sulfuric acid; and aluminum with sodium hydroxide. In a following paper[8] the results of an investigation of temperature coefficients of the separation factors in several of the reactions are presented.

In both this and the following paper the specific gravity of pure D₂O at 27° is taken to be d^{27}_{27} = 1.10768[9] and that of pure protium water with the normal oxygen isotope ratio d^{27}_{27} = 0.999982.[10] Account is also taken of the slight non-additivity of H₂O and D₂O volumes reported by Luten.[11] This makes the equation for the specific gravity of a D₂O–H₂O mixture, in terms of the absolute mole fraction of D

$$S_{27°} = 0.999982 + 0.10770\ N_D - 0.0012\ N_H N_D \quad (1)$$

While equation (1) is set up for 27°, it is applicable with high accuracy for moderate concentrations of D for the whole temperature range between 25 and 30°.

Experimental Description

(a) **The Reaction System.**—A diagram of an improved form[12] of the reaction system is shown in Fig. 1.

At the beginning of each run a weighed quantity (400–800 g.) of water, acid or base, with an enriched D content, was placed in the reaction vessel A, and a weighed quantity of the solid reagent (in small pieces) was placed in C.

(1) Except for slight modification for newer values of oxygen isotope abnormality in the electrolyte and in air and for the densities of pure D₂O and pure protium oxide, the values in this paper were presented before the Division of Physical and Inorganic Chemistry at the Cleveland Meeting of the American Chemical Society (September, 1934) and the Symposium on Deuterium, held with the Pittsburgh Meeting of the American Association for the Advancement of Science (December, 1934). Original manuscript received September 19, 1941.

(2) E. W. Washburn and H. C. Urey, Proc. Natl. Acad. Sci. U. S., 18, 496 (1932).

(3) L. Farkas and A. Farkas, Nature, 133, 139 (1934).

(4) C. O. Davis and H. L. Johnston, THIS JOURNAL, 56, 492 (1934).

(5) J. Horiuti and A. L. Szabo, Nature, 133, 327 (1934).

(6) E. D. Hughes, C. K. Ingold and C. L. Wilson, ibid., 133, 291 (1934); J. Chem. Soc., 493 (1934).

(7) L. H. Reyerson, O. Johnson and C. Bemmels, THIS JOURNAL, 61, 1594 (1939).

(8) H. L. Johnston and W. H. Hall, manuscript in preparation.

(9) H. L. Johnston, THIS JOURNAL, 61, 878 (1939).

(10) H. L. Johnston, ibid., 57, 484 (1935).

(11) D. B. Luten, Phys. Rev., 45, 161 (1934).

(12) This is actually a diagram of the reaction system used by Johnston and Hall.[8] In the original design the reaction flask was not thermostatted but was either exposed to air, or sprayed with a continuous stream of tap water (cf. seq.). The semi-automatic levelling bulbs (H, H) and calibrated flowmeters (J, J) were not included in the original design.