25 cc. of phosphorus oxychloride. After the reaction had moderated, within twenty minutes, an additional 25-cc. portion of phosphorus oxychloride was added. The mixture was stirred for an additional forty-five minutes and was maintained during this time at a temperature of 65–75°. The mixture was then cooled and poured into 50 cc. of cold water. After neutralizing the solution with sodium carbonate, the mixture was repeatedly extracted with ether until the organic layer was nearly colorless. The ether solution was filtered and the ether was removed at room temperature. The residual oily 3-chloropyridazine was used for the hydrogenation reactions without purification. The average yield was 24 g. (68%).

For purification the product was distilled at 1 mm. pressure. If the bath temperature rose to about 95°, however, the chloropyridazine decomposed rapidly, liberating a large amount of gas and leaving a carbonaceous residue in the distilling flask. The colorless distillate solidified in the well-cooled receiver but the product could not be kept for more than a few hours without extensive decomposition. Solutions of 3-chloropyridazine in alcohol appear to be relatively stable at room temperature.

Pyridazine.—A mixture of 24 g. of 3-chloropyridazine, 20 cc. of concentrated ammonia water, 50 cc. of 95% alcohol, and 0.75 g. of a palladium[7] catalyst was hydrogenated at room temperature and under an initial pressure of 45 lb. The reaction was essentially complete within fifteen to thirty minutes. The filtrate was evaporated to 70 cc. and was treated with strong aqueous sodium hydroxide. The aqueous solution was extracted four to five times with benzene. The benzene solution was dried over solid potassium hydroxide and the benzene was removed. The pyridazine distilled at 62–67° under 2–3 mm. pressure. The average yield was 5.2 g. For the spectrographic work the pyridazine was distilled at atmospheric pressure, boiling at 205–206°, and then fractionated at 1 mm. pressure, the product distilling at 47–48°. The following physical constants were determined on the spectrographic sample: d^{20}_{20}, 1.111; n^{30}_{D}, 1.5148.

The surprisingly high boiling point of pyridazine suggested the possibility that association might be detected in solution. However, a solution of 0.2137 g. of pyridazine in 23.577 g. of benzene resulted in a freezing point lowering of 0.55°, giving an observed molecular weight of 84.5 as against a calculated value of 80.0.

2-Methyl-3(2)-pyridazone.—To a mixture of 15 g. of 3(2)-pyridazone and 10 g. of methyl sulfate in 50 cc. of methanol was added, with shaking, a solution of 8 g. of sodium hydroxide in water. After one hour of refluxing the alcohol was removed and the residue was extracted with benzene. Distillation of the residue from the benzene extract at 1–2 mm. gave 2.0 g. of a hygroscopic oil which readily crystallized to a hygroscopic solid melting at 38–39°.

Anal. Calcd. for $C_5H_6N_2O$: C, 54.5; H, 5.5. Found: C, 55.0; H, 5.5.

3-Methoxypyridazine.—To a methyl alcohol solution of 12 g. of 3-chloropyridazine was added a solution made up by dissolving 3.7 g. of sodium in 40 cc. of methanol. The temperature rose to about 50° and the mixture was heated under a reflux condenser for two hours. After removal of the methanol the residue was treated with a few cc. of strong aqueous sodium hydroxide solution and extracted with benzene until the extract was colorless. The benzene solution was dried with calcium chloride, filtered, and the benzene was removed. The residue distilled at 77–78° at 5 mm. The average yield was 6.0 g. (55%), n^{30}_{D} 1.5086.

Anal. Calcd. for $C_5H_6N_2O$: C, 54.5; H, 5.5. Found: C, 54.3; H, 5.2, 5.4.

3-Ethoxypyridazine.—3-Ethoxypyridazine was obtained in 56% yield under similar conditions. The product distilled at 69–71° at 2–3 mm. and the solid melted at 35–36°. The refractive index of the liquid at 30° was 1.5000.

Anal. Calcd. for $C_6H_8N_2O$: C, 58.0; H, 6.5. Found: C, 58.2; H, 6.4.

This compound was also prepared by the reaction of 3-chloropyridazine with a solution of potassium hydroxide in 95% ethyl alcohol.

Summary

The absorption spectrum of pyridazine solutions in hexane and water from 2400 to 3800 Å. is reproduced.

Three new pyridazine derivatives have been prepared. They are 2-methyl-3(2)-pyridazone, 3-methoxypyridazine and 3-ethoxypyridazine.

BALTIMORE, MD. RECEIVED MARCH 13, 1944

---

(7) We are indebted to Dr. Walter H. Hartung of the University of Maryland for allowing us to report the method of preparation of this catalyst prior to his publication. It was prepared by hydrogenating for thirty minutes under an initial pressure of 45 lb. a mixture composed of 16.4 g. of sodium acetate, 3.0 g. of Norit A, and 3 cc. of a 10% solution of palladium chloride. The Norit was then filtered, washed with water, and dried in a stream of nitrogen at 70°. This catalyst is pyrophoric in the presence of alcohol.

[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

The Sorption of Hydrogen by Poisoned Copper. Temperature Variation Experiments

BY CARROLL W. GRIFFIN

Introduction

The effect of a small amount of carbon monoxide both upon the catalytic activity of massive copper in the hydrogenation of ethylene[1] and upon the sorption of hydrogen by this metal[2] has been established. Whereas the catalytic activity is almost completely destroyed by the poison, the 0° sorption of hydrogen is actually increased at low pressures although decreased at high pressures. Interpreting these results, the author suggested that not only physical and activated adsorption of hydrogen occurs upon copper, but, in addition, solution of hydrogen. The same conclusion was reached by Benton and White.[3] Numerous experiments have been carried out to throw further light upon this question of solubility. These have included sorption measurements with supported sorbents which could have very little accommodation for solution[4] and "experiments with temperature variation," introduced by Benton and White[3] with massive copper and extended by the writer to include supported metals.[5] These data support the belief that many

---

(1) Pease and Stewart, THIS JOURNAL, **47**, 1235 (1925).

(2) Griffin, *ibid.*, **49**, 2136 (1927).

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

(4) Griffin, *ibid.*, **57**, 1206 (1935); **59**, 2431 (1937).

(5) Griffin, *ibid.*, **61**, 270 (1939); **63**, 2957 (1941).

metals which sorb hydrogen also dissolve the gas. In such experiments the sorbate is brought into equilibrium with the sorbent at a low temperature, say −78.5°, the temperature is then elevated, for example, to 0°, and, after measuring the pressure, the temperature is returned to −78.5°. With many metals it has thus been shown that the low-temperature sorption is followed by a rapid desorption when the temperature is raised and then by the slower solution at the higher temperature. When return is made to the lower temperature the sorption is found to be greater than the original sorption at this temperature by an amount equal to the volume slowly taken up at the higher temperature.

If it is true that the hydrogen molecules must be activated before solution may take place, then the occupation of many of the most active centers of copper by carbon monoxide should largely deprive the sorbent of the capacity to dissolve hydrogen. Under such circumstances experiments with temperature variation should reveal a situation quite different from that prevailing when carried out on unpoisoned copper. The present work was undertaken to establish the behavior of hydrogen with copper which had been so poisoned.

Experimental

The apparatus,[6] the method of making a run, and the purification of hydrogen and of helium, used as a reference gas,[2] have been described. The copper sample of 80 g. was obtained by reducing copper oxide with hydrogen at 200°, reoxidizing at 200° and reducing again at 150°. In a run employing poison the carbon monoxide was introduced at the temperature of the run a half hour before admitting the first portion of hydrogen within the bulb. Usually equilibrium was approached from the low-pressure side but some checks on hysteresis were made by withdrawing hydrogen and measuring the pressure.

The sorption of hydrogen on the pure copper was first determined at −78.5° and at several pressures up to one atmosphere and then at 0°. Next a run was made on the copper poisoned with 0.039 ml. of carbon monoxide. Then three runs (evacuation between runs) with temperature variation, −78.5 to 0 to −78.5°, on the unpoisoned copper were made, and finally three similar runs with temperature variation after poisoning with 0.039 ml. of the monoxide.

Results

Isotherms with Unpoisoned Copper.—Curves 1 and 2 of Fig. 1 are the isotherms for hydrogen on pure copper at −78.5 and at 0°, respectively. Curves 3 and 4, in order, represent the activated adsorption and solution of hydrogen at 0°. The values in Row 2 of Table I give the adsorption at 0° for a given experiment (plus solution, if any, at −78.5°). The differences in Row 4 are the volumes of hydrogen dissolved at 0° at pressures of Row 2, while the differences in Row 8 are the volumes dissolved at 0° at pressures of Row 5. The sums of adsorption and solution are found in Rows 3 and 5.[3] Curves of the same general character as 1, 2, 3, and 4 have already been obtained[3]; these isotherms confirm the solution of a considerable amount of hydrogen in unpoisoned copper.

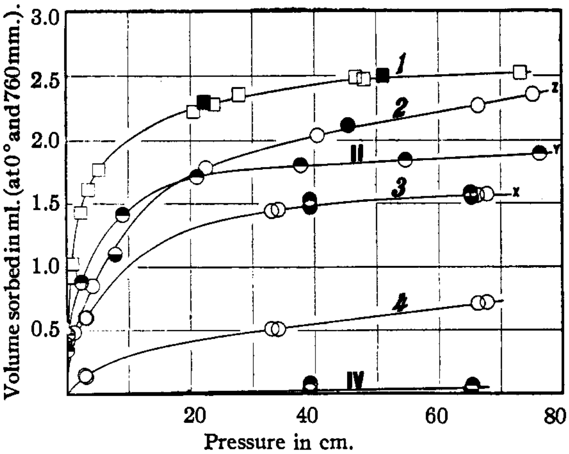

Fig. 1.—Sorption of hydrogen on massive copper. Curve 1, total sorption at −78.5° with either unpoisoned copper or copper after poisoning with 0.039 ml. of CO; 2, total sorption at 0°; II, sorption at 0° after poisoning with 0.039 ml. of CO; 3, adsorption at 0°; 4, solution at 0° in unpoisoned copper; IV, solution at 0° in copper after poisoning with 0.039 ml. of CO.

TABLE I

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF HYDROGEN BY 80 G. OF MASSIVE COPPER

(1) Gas taken up at −78.5°	Press.	22.2	236.1	481.1
	Vol.	1.43	2.29	2.48
(2) Initial values after warming to 0°	Press.	32.2	341.4	678.6
	Vol.	0.60	1.45	1.57
(3) Total sorption at 0° at pressure given in (2)		0.74	1.96	2.29
(4) Differences of (2) and (3)		0.14	0.51	0.72
(5) Final values reached at 0°	Press.	30.8	330.9	663.6
	Vol.	0.84	1.94	2.27
(6) After cooling to −78.5°	Press.	22.0	228.3	470.3
	Vol.	1.55	2.79	3.17
(7) Direct values at −78.5° at pressures given in (6)		1.42	2.28	2.46
(8) Differences of (6) and (7)		0.13	0.51	0.71

Isotherms with Poisoned Copper.—Three points of Curve I were obtained at −78.5° after the sorbent had been poisoned with 0.039 ml, of carbon monoxide. These points fall upon or very close to the curve established by points of the pure run at −78.5°. Curve II is the isotherm secured at 0° after poisoning. This curve crosses Curve 2 as previously has been found[2] and shows the expected low-pressure increase and high-pressure decrease in sorption due to the monoxide. Curve IV reveals a slight solution of hydrogen found for the copper after poisoning.

It will be noted that Row 4 of Table II gives a measure of solution in the poisoned copper just as surely as does Row 4 of Table I for pure copper. In the latter case the values of Row 4, Table I, are obtained by subtracting from a given volume in Row 3, representing adsorption plus solution, the corresponding volume in Row 2, representing ad-

---

(6) Pease, THIS JOURNAL, 45, 1196 (1923).

sorption alone. In the case of poisoned copper Row 4 of Table II also measures solution, for here a total sorption of Row 3 represents the sum of adsorption plus the low-pressure increase plus solution, if any; Row 2 here represents adsorption plus low-pressure increase. The further check on the extent of solution, Row 8 of Table II, might have been complicated by the low-pressure increase in adsorption occurring while the sorbent was at 0°. Had the calculations of Row 8 for poisoned copper yielded results much higher than those of Row 4, such would have pointed to a retention of the 0° low-pressure increase under −78.5° conditions. However, since Row 8 yields volumes for solution which, with one exception, closely check the values of Row 4, the conclusion is justified that the 0° low-pressure increase in adsorption is given up when the temperature is lowered to −78.5°, the activated adsorption at this lower temperature resuming its normal value.

Table II

Effect of Changing Temperature on Sorption of Hydrogen by 80 g. of Massive Copper Poisoned with 0.039 ml. of Carbon Monoxide

(1) Gas taken up at −78.5°	Press.	51.2	267.8	466.6
	Vol.	1.77	2.36	2.49
(2) Initial values after warming to 0°	Press.	78.5	392.9	653.9
	Vol.	1.38	1.72	1.80
(3) Total sorption at 0° at pressures given in (2)		1.35	1.80	1.86
(4) Differences of (2) and (3)		−0.03	0.08	0.06
(5) Final values reached at 0°	Press.	78.5	392.3	652.9
	Vol.	1.38	1.75	1.85
(6) After cooling to −78.5°	Press.	51.4	276.5	466.1
	Vol.	1.76	2.38	2.52
(7) Direct values at −78.5° at pressures given in (6)		1.77	2.36	2.49
(8) Differences of (6) and (7)		−0.01	0.02	0.03

To secure the points for Curve 3, the activated adsorption, with data from poisoned copper, it is, of course, necessary to take the difference between the sorption given by the isotherm (Curve II) and the solution plus low-pressure increase, and not simply, as in the case of pure copper, the difference between the isotherm (Curve 2) and solution alone. For the sorbent of this study the value of 0.25 ml. was taken as the low-pressure increase since 0.25 ml. is seen from Fig. 1 to be the volume at most pressures, including zero pressure, by which Curves II and 3 differ, Curve 3 having already been established from runs with the unpoisoned copper.

In the present investigation, by obtaining Curve 3 in addition to Curve II, the first experimental evidence is secured for the parallel nature of Curves X and Y of Fig. 6 of an earlier study.[2] In the latter figure Curve Z corresponds to Curve 2 of the present work.

The rate of attaining equilibrium for hydrogen on pure copper was rather slow, resulting only after four or five hours. Both for 0 and for −78.5° there is some evidence of hysteresis as seen in Curves 1 and 2 (full black symbols). At low pressures however no pressure change was noted after a half hour. Equilibrium resulted more quickly on the poisoned copper, due to the almost total absence of solution, 90 to 150 minutes being sufficient.

Summary

The sorption of hydrogen with temperature variation on pure massive copper has been determined and compared with that of hydrogen on the same copper poisoned with a small quantity of carbon monoxide. The effect of the poison is to prevent largely the solution of hydrogen in copper.

Poughkeepsie, N. Y.

Received October 3, 1944

[Contribution from the Chemical Laboratories of New York University]

Dimorphism in Aluminum Fluoride Trihydrate(1)

By W. F. Ehret and F. J. Frere

In connection with our study of ternary systems involving aluminum fluoride, a report of which appears elsewhere,[2] it became necessary to investigate the structure, the extent of hydration, and the solubility of the stable form of aluminum fluoride at 25°. This necessity arose out of conflicting statements about this salt in the literature and, further, out of slow changes with time which we noticed in the solubility and other properties of the salt as usually prepared. One is led to believe from the statements found in the literature that aluminum fluoride exists in a soluble and an insoluble form, the soluble form being prepared at low temperature. The latter is said not to undergo any change with time, providing there is no appreciable rise in temperature.

According to Baud[3] and Mazzucchelli,[4] when two volumes of 95% alcohol are added to a neutral solution of alumina in hydrofluoric acid, a crystalline precipitate of $AlF_3{\cdot}3.5H_2O$ is obtained. Baud states that the salt precipitates first in the form of an oil which, upon standing, crystallizes. The above authors state that another form of hemiheptahydrated aluminum fluoride, almost

---

(1) Abstracted from a thesis submitted by Francis J. Frere to the Graduate School of New York University in partial fulfillment of the requirements for the degree of doctor of philosophy.

(2) Ehret and Frere, This Journal, **67**, 68 (1945).

(3) Baud, *Ann. chim. phys.*, (8) **1**, 60 (1904).

(4) Mazzucchelli, *Atti Accad. Lincei*, (5), **16**, 775 (1907).