In order to prove the above, the following experiments were made: 5 ml. of the normal silver nitrate solution was treated in bulb B (Fig. 1) with 10 ml. of normal sodium hydroxide. The precipitated silver oxide was washed by decantation, to free it from nitrate, and 10 ml. of N sodium hydroxide and sufficient saturated sodium sulfite solution to dissolve it (15 ml.) were added. The bulb B was attached to the apparatus, evacuated with shaking and allowed to stand. The silver was then precipitated with hydrochloric acid, the silver chloride filtered off and the filtrate boiled with hydrochloric acid until the sulfur dioxide was expelled. The sulfate content was determined as barium sulfate. The solution treated in this manner, to determine the amount of oxidation by the air or direct reduction of the silver salt, showed an increase of 0.0397 g. of barium sulfate over the amount obtained (0.3800 g.) from 15 ml. of the untreated sulfite solution. Another experiment was made in the same manner except that after the apparatus was evacuated, 50 ml. of the hydroxylamine solution was added and allowed to react. After filtering off the precipitated silver, the solution was boiled with hydrochloric acid and the sulfate determined. This showed an increase of 0.3744 g. of barium sulfate over the amount in the original sulfite solution or an increase of 0.3374 g. due to the induced reaction.

If the previously mentioned reaction occurs, then 57.4% of the silver nitrate is reduced by the sodium sulfite. In the previous experiments (Table III) a yield of 36.7% of nitrogen was obtained, which together with the above gives a total of 94.1%, similar to that obtained in the other experiments. These results indicate that the silver salt is reduced by both the hydroxylamine and the sodium sulfite due to a coupled or induced reaction. The last experiment in Table II indicates that with ammoniacal silver nitrate no induced reaction occurs or, at least, only a very small amount of the reduction is due to sodium sulfite.

Summary

1. The gaseous products of the action of hydroxylamine on silver salts were determined.

2. Silver bromide in the presence of sodium hydroxide gives a mixture of nitrous oxide and nitrogen.

3. Ammoniacal silver nitrate gives pure nitrogen.

4. Alkaline silver nitrate in the presence of sodium sulfite gives a mixture of nitrous oxide and nitrogen.

5. When hydroxylamine reacts with alkaline silver nitrate in the presence of sodium sulfite, a coupled or induced reaction occurs.

6. The composition of the gaseous products varies with the strength of the alkali and the temperature.

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

The Adsorption of Hydrogen by Copper Poisoned with Cyanogen

BY CARROLL W. GRIFFIN

Several years ago Pease[1] found that at 0° both the adsorption of hydrogen and of ethylene on copper and the catalytic activity of the metal toward an ethylene–hydrogen mixture suffered a marked decrease either by heating the copper to moderately high temperature or by poisoning it with a small quantity of mercury. Especially in the low-pressure region was the decrease in adsorption great and at the time it appeared that a correlation existed between catalytic activity and the strong or low-pressure adsorption of the reactants. Later Pease and Stewart[2] revealed that the catalytic activity of a copper catalyst was much reduced for the hydrogenation of ethylene by poisoning the catalyst with a minute quantity of carbon monoxide. With this poison, however, adsorption measurements[3] showed that a trace of carbon monoxide on the copper causes a low-pressure increase which gives way to a high-pressure decrease in the adsorption of both hydrogen and ethylene at 0 and at 20°. This result was interpreted by supposing the sorption of the gases to comprise two or more processes one of which was thought to be solution.

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(1) Pease, THIS JOURNAL, **45**, 2296 (1923).

(2) Pease and Stewart, *ibid.*, **47**, 1235 (1925).

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

Benton and White[4] have recently found that a small amount of carbon monoxide on nickel likewise causes an increase in the adsorption of hydrogen by this metal at 0° but the increase persists up to one atmosphere pressure. Apparently the isotherm would cross that of the hydrogen on unpoisoned nickel if measurements were carried to higher pressure. If so then the behavior of the poison on the two metals would be qualitatively similar.

Inasmuch as it seemed likely that carbon monoxide forms a complex with hydrogen in the presence of active copper and nickel, thus accounting for the increase in hydrogen adsorption, it was thought desirable to experiment with another gaseous poison. Dr. A. F. Benton some time ago, in conversation with the writer, suggested that cyanogen might prove an interesting case.

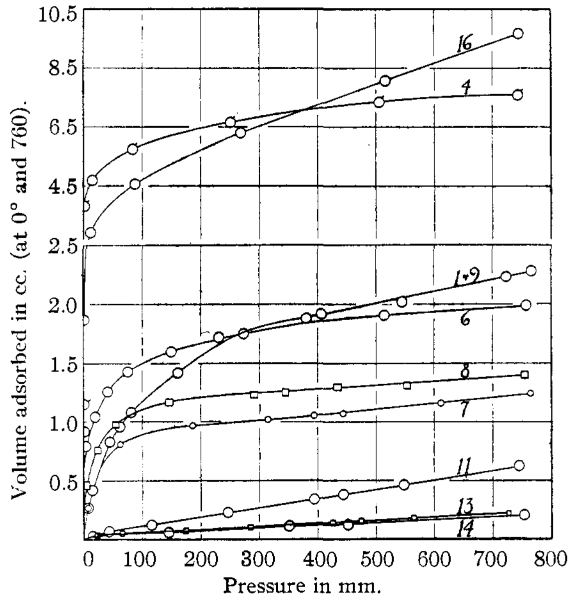

Fig. 1.—Adsorption of hydrogen on copper poisoned with carbon monoxide and with cyanogen at 0° (change in volume scale after 2.5 cc.): Curve 14, H_2 with 0.88 cc. C_2N_2; 13, H_2 with 0.34 cc. C_2N_2; 11, H_2 with 0.043 cc. C_2N_2; 7, H_2 with 0.91 cc. CO; 8, H_2 with 0.31 cc. CO; 6, H_2 with 0.043 cc. CO; 1 (and check run 9) H_2 with no poison; 4, pure CO; 16, pure C_2N_2.

Experimental Part.—Preliminary tests showed that cyanogen is adsorbed to a considerable extent by copper at 0°. Although it was found impossible to pump off at 200° all the adsorbed cyanogen, nevertheless the progressive effect of this poison could be studied by increasing the quantity of the cyanogen in successive runs. In order that the results should be indisputably comparable with those obtained when carbon monoxide is used as the poison, three runs were made in this investigation using the monoxide poison, and these were followed by the adsorptions of hydrogen on the catalyst poisoned with cyanogen. These three runs made with the monoxide poison confirm the results previously obtained.[3]

The apparatus was similar to that employed by Pease[5] with two exceptions. First, gas volumes were determined as described by Benton and White.[6] Second, the stopcock leading to the bulb containing the copper was a specially constructed three-way, mercury-sealed stopcock. The method of preparation of the hydrogen and the carbon monoxide, and the limits of accuracy have been described previously.[3] The method of measuring the smallest volume of poison has been explained.[7] Cyanogen was prepared by heating dry mercuric cyanide. The 117.4 g. of copper was obtained by reduction of copper oxide in wire form at 200° followed by oxidations and reductions at 175 and 150°. Helium was used as a reference gas (Run 2). The reversibility of high-pressure adsorptions was confirmed in each run by the absence of hysteresis. Between runs the catalyst bulb was evacuated at 200°.

Results.—Runs are numbered in the order in which they were made and the curves of the figure are numbered to correspond to the runs. The adsorption isotherms are shown in Fig. 1. Curves 6, 8 and 7 were obtained with carbon monoxide as the poison and are given for comparison with curves 11, 13 and 14 which show the effect of cyanogen. These curves show that the effect of the latter as a poison is to decrease the hydrogen adsorption, particularly in the low-pressure region. Thus its effect is distinctly different from that of carbon monoxide and is similar to that of mercury poisoning and of heat treatment. The carbon monoxide effect is then, as far as data now accumulated show, still unique. It has been shown previously[3] how this effect may be explained by assuming a secondary action in addition to that of straight adsorption. It was pointed out that this secondary action may be solution of the hydrogen in copper. Now if such is the case, or if, instead, a diffusion of hydrogen into the copper takes place, then the secondary

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

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

(6) Benton and White, *ibid.*, **52**, 2327 (1930).

(7) Griffin, *Chemist-Analyst*, **19**, 21 (1931).

action would be almost negligible at low pressure, and since either solution or diffusion would be slower in attaining the equilibrium condition than surface adsorption, it follows that the rate of sorption on unpoisoned copper ought to be faster at low pressure than at higher pressures. Furthermore, if, as previously proposed, the poison prevents the secondary action, it follows that the rate of sorption on poisoned copper should be faster than on unpoisoned copper.

It therefore is of interest to note that the following points concerning rate of sorption have been found to hold generally in this study. First, the rate of sorption of hydrogen on unpoisoned copper is rapid at low pressures and becomes progressively slower as the pressure ascends. Second, at higher pressures equilibrium is reached somewhat more quickly as a result of poisoning both by carbon monoxide and by cyanogen. Each of these observations may thus be interpreted to mean that the sorption is due in part to the secondary factor and that it, a slower process, manifesting itself more at higher pressures, is inhibited by the poisons. Apparently both carbon monoxide and cyanogen possess this inhibitory property but the former in addition is able to form a complex with hydrogen in the presence of copper (thus giving the low-pressure increase) while the latter is not.

From time to time during this study the catalytic activity of the copper was tested, using 1:1 mixtures of hydrogen and ethylene at 0° (Runs 3, 5, 10, 12, 15 and 17). The activity remained satisfactorily stable up to the time cyanogen was first employed, namely, 100% in Run 3, 103.2% in Run 5 and 101.6% in Run 10. After the first use of cyanogen in Run 11 the catalytic activity in Run 12 had fallen to 15.3%, in Run 15 to 0.3% and in Run 17 to practically zero. This indicated that at least a part of the cyanogen was not pumped off after Run 11 and signified the deactivating power of cyanogen. As a result of this observation the gas pumped off at the conclusion of Run 14 was measured. In this run 0.88 cc. of cyanogen had been admitted to the bulb one-half hour before the sorption of hydrogen was started. The amount pumped off was 0.8 cc. less than the total volume, cyanogen plus hydrogen, added. This shows the difficulty of removing cyanogen from copper at 200° and further implies that the amount of poison acting in Run 14 was greater than the 0.88 cc. admitted immediately before the run was made, *i. e.*, doubtless much or all of the 0.34 cc. of cyanogen used as a poison for Run 13 had not been pumped off at the conclusion of that run. This, however, does not detract from the information secured concerning the general character of the poisoning effect. It also means that curve 16, representing the adsorption of cyanogen itself, in order to show the total adsorptive power of this sample of copper toward cyanogen, should be shifted horizontally to the right by possibly about 1.2 cc. This would make its adsorption almost the same as that for carbon monoxide up to 100 mm. pressure and greater thereafter.

The gas pumped off after Run 16 amounted to 0.6 cc. less than the volume of cyanogen admitted. Had the surface of the copper been perfectly free from cyanogen at the beginning of the run instead of having many of the active centers already occupied by the poison, irrecoverable from Runs 14 to 11, doubtless more than 0.6 cc. would have remained unrecovered from Run 16.

Summary

1. Adsorption measurements have been made at 0° for hydrogen on a copper catalyst poisoned with cyanogen.

2. It has been found that the poison decreases the adsorption of the hydrogen, notably in the low-pressure region.

3. The effect of the cyanogen has been compared with that of carbon monoxide.

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