THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF $\frac{1}{2}$ U. S. N. P. No. 1, NITRATE
DIVISION, ORDNANCE DEPARTMENT, U. S. A.]

**THE ABSORPTION OF CARBON MONOXIDE BY CUPROUS
AMMONIUM CARBONATE SOLUTIONS.¹**

BY WM. R. HAINSWORTH AND E. Y. TITUS.

Received June 5, 1920.

The greater portion of the carbon monoxide in the gas mixtures used in synthetic ammonia processes can be oxidized catalytically to carbon dioxide and the latter removed by solution in water. Complete elimination of carbon monoxide is necessary, however, since most catalysts for the synthetic ammonia reaction are poisoned cumulatively by very small amounts of this gas. To remove the last portions completely, a direct absorbent has been found necessary. Solutions of ammoniacal cuprous chloride have proved to be unsatisfactory, owing to the tendency toward deposition of the copper and the gradual solution of the iron walls of the containing vessel. These tendencies are greatly reduced, however, if instead of the chloride, an ammoniacal cuprous salt of an organic acid, such as formic or carbonic acid, is used.

In order to extend our knowledge of cuprous ammonium carbonate solutions as absorbents for carbon monoxide, the investigation described in the following pages was carried out. Since, in technical mixtures, the amount of the gas which must be removed by direct

¹ Published by permission of the Chief of Nitrate Division, Ord. Dept., U. S. A.

absorption is only a small percentage of the total volume, a study of the pure gas at low pressures served to indicate its behavior in the mixtures at high total pressures. For instance, the solubility of pure carbon monoxide at a pressure of 2.0 atmospheres will approximate closely that of the same gas when it constitutes 2.0% of a gaseous mixture which is under a total pressure of 100 atmospheres.

Materials.

The carbon monoxide was obtained from the interaction of formic and sulfuric acids and was collected over sodium hydroxide solution. Analyses of the gas were made in a standard Orsat gas analysis apparatus, using the combustion method to check the carbon monoxide content determined by absorption in ammoniacal cuprous chloride solution.

The copper solutions were prepared by agitating, with air, a solution containing approximately 15% of ammonium carbonate and 5% of ammonium hydroxide by weight, in a tower filled with copper turnings until the total copper content of the solution was about 3.5%. The air was then turned off and the solutions agitated in the tower until the cupric copper present was reduced.

We will assume that 4 moles of ammonia were associated with one mole of cupric copper in the first stage of the preparation, as high ammonia concentrations were used.¹ It is possible that the concentration of ammonia was large enough to cause the formation of a small amount of a complex containing 5 or even 6 moles of ammonia, but for our purpose the equation representing the formation of the cupric salt may be written,

Very little work has been done on the determination of the ammonia association number for complex cuprous salts. It is very probable that this number is dependent on the ammonia concentration, as will be discussed later on. Since it is not known that the formation of the cuprous ammonia cation is independent of the total ammonia concentration, the reduction of $\text{Cu}(\text{NH}_3)_4\text{CO}_3$ must be represented by the equation

The total copper was determined iodometrically, the copper in the cupric state by a colorimeter, and the total ammonia content by the Kjeldahl method. The carbon dioxide was obtained by absorbing, in standard barium hydroxide solution, the gas evolved from the acidified solution, and titrating the excess of alkali.

Apparatus and Manipulation.

Apparatus A.—This apparatus, shown diagrammatically in Fig. 1, was used to determine the absorption curves, *i. e.*, curves showing the re-

¹ Locke and Forsall, *Am. Chem. J.*, **31**, 268 (1904); Dawson, *J. Chem. Soc.*, **89**, 166 (1906).

lation between the volumes of carbon monoxide absorbed per volume of solution at temperatures ranging from 1 to 40° and pressures from 0.3 to 4.0 atmospheres. The pressure of the gas in the 100 cc. eudiometers A and B and over the copper solution contained in the U-tube D, was controlled by raising and lowering the mercury leveling Bulbs C, and was read with an accuracy of one mm. by means of the meter sticks F, the portion of these sticks under water being varnished and paraffined to prevent lengthening by water absorption. The temperature was maintained constant within 0.1° by immersing the entire apparatus in a glass windowed thermostat, allowing the eudiometers to project far enough through the stoppers in the bottom to afford adequate fastening for the heavy rubber tubing used. Gas was introduced or removed, as desired, by means of the 2-way Stopcock G and the copper solution was placed in the U-tube through the stopcock E, the short piece of capillary tubing above it then being filled with mercury.

Fig. 1.

It is evident that in the apparatus above described, the actual pressure of the carbon monoxide above the solution was equal to the total or observed pressure minus the pressure of the gases from the solution, namely, ammonia, water vapor, and carbon dioxide. The latter pressure, which in this paper will be called the vapor pressure of the solution, was separately determined, thus necessitating the assumption in subsequent calculations that the comparatively small amount of carbon monoxide absorbed by the solution does not appreciably lower the vapor pressure of the solution. The vapor pressures were determined by introducing a small quantity of each solution into the vacuum of a mercury barometer and noting the drop of the meniscus. In use, the barometer was immersed in the thermostat, correction being made for the weight of the water column.

Manipulation.—A volume of carbon monoxide was brought into Apparatus A by first filling it completely with mercury which was then displaced by the gas. Temperature, pressure, and volume readings were then taken under several different conditions and checked by reducing to standard conditions (0° and 760 mm.).

A known quantity of copper solution was next introduced through Stopcock E. This was accomplished by means of a 10-cc. pipet, to one end of which a 2-way capillary stopcock was joined, a mercury leveling bulb being attached to the other end. The copper solution was drawn into the pipet without exposure to air, and a certain amount forced into

the absorption apparatus. By reading the mercury meniscus in the pipet before and after introducing the solution, the exact volume of the solution was obtained. The solution remaining in the stopcock E and capillary was displaced by mercury from the leveling bulb, after discarding the excess solution in the pipet.

The volume of gas which remained, after equilibrium with the copper solution at a given pressure and temperature had been established, was obtained by reading the volume in the eudiometers and adding to it the volume in the U-tube which had been previously calibrated. Equilibrium volumes were obtained by first regulating the thermostat to the desired temperature and then reducing the pressure as far as possible by lowering the leveling bulbs C C, Fig. 1, without allowing the gas to enter the rubber tubing. The system was then allowed to stand until it was evident that no more gas would come out of solution. The pressure was next increased to the equilibrium pressure desired and the gas was bubbled back and forth through the solution by a slight raising of one of the bulbs and a corresponding lowering of the other, and *vice versa*. By bubbling the gas through the liquid 4 or 5 times every 10 minutes, equilibrium was established in several hours. Readings were taken at intervals during this time, and successive corrected volumes compared. When it was found that these volumes did not vary more than 0.2%, it was assumed that equilibrium for that particular pressure and temperature had been attained. In the above manner equilibrium values were obtained for a given pressure approaching from the low pressure side. It was repeatedly found that by bringing the system back from high pressures to pressures and volumes at which measurements had previously been made, the same volume of gas was read off on the eudiometers. In other words, the absorption of carbon monoxide by the solutions used was found to be reversible.

For reduced pressures, such an amount of gas was removed, by means of the stopcock at the base of the eudiometer, that the highest equilibrium pressure obtainable with the remaining gas volume fell within the limits of the lowest equilibrium pressure obtainable with the original gas volume. Thus the curve showing the relation between pressure and volumes of carbon monoxide absorbed per volume of solution, was made a continuous one. For pressures below 50 cm. of mercury it was necessary to dilute the carbon monoxide with nitrogen, and then remove some of the resultant mixture. Tank nitrogen from which the oxygen had been removed was used. The solubility of nitrogen in the copper solutions, although very small, is not known and introduces a slight error in the low pressure values.

Apparatus B.—Owing to difficulties discussed later on, it was not possible to use the apparatus described above for temperatures over 40°.

In consequence, a simple apparatus was used which consisted of an inverted buret containing the copper solution and gas over mercury. The pressure was controlled by means of a leveling bulb similar to C, Fig. 1, and the temperature was regulated by circulating water through a jacket surrounding the buret.

Manipulation.—A sample of copper solution was drawn into the buret without exposure to air, and saturated with carbon monoxide at room temperature and pressure. The temperature was raised to 40° and maintained constant until equilibrium between the gas and solution had been established, when the excess gas was discarded through the upper stopcock. The temperature was next raised to another definite point, the volume of gas evolved by raising the temperature was noted, and the gas subsequently discarded. Equilibrium at each temperature was tested either by increasing the pressure and then allowing the gas to come out of the solution by lowering the pressure to one atmosphere, or by first reducing the pressure and then forcing the gas into the solution by raising the pressure to one atmosphere. This process of raising the temperature by intervals was repeated up to 85° , the decomposition temperature of ammonium carbonate.

Experimental Results.

Three experiments were made on copper solutions of the following compositions.

	G. Per 100 Cc.	
	Expt. 1.	Expt. 2
Total copper.....	3.89	4.79
Total CO_2	4.73	6.11
Total NH_3	4.69	11.60
Cuprous copper.....	3.89	4.57
Cupric copper.....	Trace	0.22

Expt. 1.

A volume of 424 cc. (0° and 760 mm.) of dry gas analyzing $\text{CO} = 98\%$, $\text{O}_2 = 0.4\%$, and $\text{N}_2 = 1.6\%$ was introduced into the absorption Apparatus A. Following this, 6.5 cc. of the copper solution was added, resulting in the immediate oxidation of a very small amount of the copper, which was subsequently reduced again by the carbon monoxide, thus producing a colorless solution in about half an hour. When the reaction $2\text{CO}_2 + \text{O}_2 = 2\text{CO}$ (dissolved) took place, the initial volume was reduced to 418.9 cc. of gas having a carbon monoxide partial pressure of 0.984.

The following data for Point 8, Fig. 2, illustrates the method used to establish points on the equilibrium curves given in Figs. 2 and 3.

Total gas vol. = 138.8 cc.; temp. = 6° ; Hg Col. = 1222.5 mm. Barometer = 750.6 mm.; V. p. of copper solution = 16 mm. This gives 10.62 vol. of CO per vol. of solution at 1925.5 mm. of Hg, CO pressure.

The points on the curves are numbered consecutively as taken to show the direction from which the equilibrium point was reached. The data taken in Expt. 1 are plotted in Fig. 2.

Fig. 2.

Expt. 2.

The gas mixture in this experiment analyzed $\text{CO} = 99.75\%$, $\text{O}_2 = 0.05\%$, $\text{N}_2 = 0.20\%$, and the following corrections on the initial volume of 290.6 cc. were made, using Apparatus A and 6.6 cc. of solution. Since the specific gravity of the solution was very close to 1.0, there was $0.0022 \times 6.6 = 0.0145$ g. of cupric copper present, which upon reduction to cuprous copper by CO caused the removal of 2.55 cc. of gas

Fig. 3.

as dissolved carbon dioxide. The presence of 0.05% of oxygen in the gas caused a reduction in volume of 0.4 cc., therefore the total gas volume at the start was 287.6 cc. having a CO partial pressure of 0.998.

The data taken in Expt. 2 are plotted in Fig. 3. Above 40° a noticeable amount of copper progressively precipitated as a mirror from the solution. The reduction necessarily was accompanied by the oxidation of some carbon monoxide, which resulted in a decrease in gas volume, as the carbon dioxide produced remained in solution. The points on the curve at 40° and above are, therefore not as accurate as those determined for the curves at lower temperatures.

Expt. 3.—The purpose of this experiment was to obtain data on the regeneration of the copper solution after it had been used as a carbon monoxide absorbent. The regeneration can be accomplished by heating the used solution in a container at atmospheric pressure, without exposure to air, thereby driving out the carbon monoxide.

The experiment was carried out in Apparatus B, with a sample of the same solution as that used in Expt. 2, but at temperatures above 40°. To obtain from Expt. 2 the equilibrium points for temperatures below 40°, at a total pressure of one atmosphere, it is only necessary to subtract the vapor pressures of the solution at the different temperatures from one atmosphere, and read the corresponding volumes of CO absorbed (Fig. 3).

Fig. 4 summarizes the results of the 2 experiments and shows the effect of temperature on the volumes of carbon monoxide absorbed per volume of solution under a total pressure

Fig. 4.

of one atmosphere. The values obtained in Expts. 2 and 3 are represented by crosses and circles, respectively.

Chemical Reactions between Copper Ammonium Carbonate Solution and Carbon Monoxide.

I. Reduction by Carbon Monoxide.

Observations on the behavior of the copper solutions in the experiments outlined above, and the results of tests on the comparative rates of reduction by carbon monoxide of solutions varying in total copper and free ammonia content are summarized below. The tests on the rates of reduction were made by saturating the solutions in bulbs with carbon monoxide, and noting the progressive decolorization of the solution or the

precipitation of copper. Since the carbon monoxide was continuously oxidized in solution, the bulbs were connected to a constant supply of the gas at atmospheric pressure.

A. The reduction of cupric copper by carbon monoxide, takes place fairly rapidly according to the equation.

and is hastened by heating. Since no oxalates were found in the solutions, it is assumed that the carbon monoxide was oxidized to carbon dioxide, and that the oxidation did not stop at an intermediate stage. In general it was found that, with occasional agitation, solutions with a total copper content of 1 to 5% and containing not over 1% cupric copper in the presence of an excess of ammonia would become colorless within an hour at room temperature, and within less than 10 minutes at 60°.

B. The reduction of cuprous copper to metallic copper as illustrated by the equation

is comparatively slow at room temperature, but is also hastened by heating. Solutions having approximately 5% total copper present in the cuprous state, and an excess of ammonia, precipitated a noticeable amount of copper within 48 hours, while solutions with only 1% total copper as cuprous copper, under the same conditions, required over a month before the precipitate was noticeable. That the reduction was due to the presence of carbon monoxide, and not to simple decomposition, was shown by the fact that duplicate samples which were not treated with carbon monoxide produced no precipitate under the same conditions.

C. The presence of a small amount of oxygen gas in the gaseous mixture used in a continuous process, and from which carbon monoxide is to be removed by absorption in the copper solution, tends to prevent the precipitation of copper from the solution. This follows from the consideration of the high rate of oxidation of cuprous copper to cupric by oxygen, and from the fact that the reduction of cupric copper to cuprous copper by carbon monoxide takes precedence over the reduction of cuprous copper to metallic copper by the same gas. Furthermore, the absorption capacity of the solution is increased by the presence of small amounts of oxygen, as an equivalent amount of carbon monoxide is oxidized to carbon dioxide and remains in the solution. The disadvantage is, of course, that the free ammonia content of the solution is continuously depleted by combination with the carbon dioxide formed. A high concentration of oxygen could not be used since the reduction of cupric copper by car-

bon monoxide is much slower than the oxidation of cuprous copper, and an excess of cupric copper would soon result.

2. Moles of Carbon Monoxide Absorbed Per Mole of Cuprous Copper.

The slopes of the isothermal absorption curves obtained in Expts. 1 and 2 decrease as the pressures increase. This, combined with the fact that the solubility of carbon monoxide in water is very small, indicates that the true physical solubility of carbon monoxide in the solutions at low pressures is small in comparison to the amount absorbed by the solutions. Therefore, in the following discussion, the uncombined carbon monoxide in solution is not considered, as it is less than 0.1% of the amount absorbed. The curves for the lowest temperatures studied appear to become asymptotic to a line corresponding to one mole of carbon monoxide absorbed per atom of copper. The ordinate of this line is, 13.7 and 16.9 in Expts. 1 and 2, respectively, while the maximum observed values are 11.9 and 16.8. It appears that, at the maximum pressures and lowest temperatures studied, the greater part of the carbon monoxide absorbed was probably due to the formation of an unstable additive compound,

similar in some respects to the compound obtained with cuprous chloride, which, in the solid state, has the formula $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$.¹ It is very probable that at higher pressures and lower temperatures, a less stable, higher complex would be formed.

3. Effect of Ammonia Concentration.

In the preceding pages we have assumed, for the sake of simplicity, that a fixed number, n , moles of ammonia were associated with one gram atom of copper in the cuprous ammonia complex ion. This assumption is hardly a valid one, however, as it has been fairly well established that the ammonia number in the cupric complex ion is dependent on the concentration of free ammonia in solution² and similar phenomena are to be expected in solutions containing the cuprous complex ion. A comparison of the relative amounts of carbon monoxide absorbed by the 2 solutions used in Expts. 1 and 2 at a given partial pressure of carbon monoxide, shows clearly that the solution of higher free ammonia concentration (Expt. 2), has the higher absorption capacity. This is in accordance with the fact that the absorptive capacity of cuprous chloride solutions is increased by decreasing the acid concentration.³

The equilibrium constant for the reaction,

¹ W. Manchot and J. N. Friend, *Ann.*, **359**, 100-28 (1908).

² Dawson, *J. Chem. Soc.*, **89**, 1666 (1906); Bonsdorff, *Ber.*, **36**, 2322 (1903); Bonsdorff, *Z. anorg. Chem.*, **41**, 132 (1904).

³ W. Manchot and J. N. Friend, *Ann.*, **359**, 100-28 (1908).

where x is a variable, dependent on free ammonia concentration, can be evaluated by making use of the condition equation,

$$[\text{Cu}^+] + [\text{Cu}(\text{NH}_3)_x^+] + [\text{Cu}(\text{NH}_3)_x.\text{CO}^+] = \text{total copper}, \quad (7)$$

in which the concentration of the cuprous ion is negligibly small, and the concentration of $[\text{Cu}(\text{NH}_3)_x.\text{CO}^+]$, practically equal to the concentration of the carbon monoxide absorbed by the solution. Although the values calculated for the constant at 11° , decrease by approximately 15% between 0.25 and 2.5 atmospheres in Expts. 1 and 2, the constant obtained in Expt. 2 is close to 8.5 times larger than that obtained in Expt. 1, at any given partial pressure of carbon monoxide.

The above facts indicate that, under the conditions of the experiments, the cuprous complex with the higher value of x has a greater affinity for carbon monoxide. The results, however, are only qualitative, and the exact nature of the effect of ammonia cannot be determined in the above manner, due to the probable existence of several ammonia complexes in the solution at once.

4. Regeneration of the Copper Solution.

It can be readily seen from Fig. 4 that the carbon monoxide absorbed at room temperature, or lower, can be practically entirely removed from solution by heating to 70° at atmospheric pressure. Although data were obtained on only one copper solution, it is reasonable to assume that the general shape of the curves would be the same for other solutions having different copper concentrations and an excess of free ammonia. The upper temperature limits would be practically the same for all solutions, as the decomposition temperature of ammonium carbonate is 85° . Since the curve tends to flatten out at low temperatures, it is apparent that cooling the solution much below room temperature does not offer a very great advantage for absorption purposes, when an excess of ammonia is present. It has been found that solutions used for absorption purposes at temperatures as low as 5° are not appreciably affected, so far as absorption capacity is concerned, by regenerating at 70° .

Summary.

1. The volumes of carbon monoxide absorbed per volume of solution have been determined at various temperatures and pressures for 2 different cuprous ammonium carbonate solutions.
2. The absorption capacity of a solution having a given cuprous copper content, is dependent on the free ammonia content of the solution and the partial pressure of the carbon monoxide above it, as well as the concentration of the cuprous copper.
3. The absorption takes place, due to the formation of an unstable compound in solution, probably containing one mole of carbon monoxide per gram-atom of cuprous copper, under the conditions studied.

4. Cupric copper is reduced to cuprous copper fairly rapidly by carbon monoxide, but the reduction of cuprous copper to copper is comparatively much slower. Oxygen present in small amounts, in gaseous mixtures from which carbon monoxide is to be removed by absorption, will prevent the precipitation of copper and increase the absorption capacity of the solution.

5. Practically complete removal of carbon monoxide from used cuprous ammonium carbonate solutions can be effected by heating to 75° at atmospheric pressure in an inert atmosphere, without decreasing the absorption capacity of the solution.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY.]

THE DEVITRIFICATION OF GLASS, A SURFACE PHENOMENON. THE REPAIR OF CRYSTALLIZED GLASS APPARATUS.

BY ALBERT F. O. GERMANN.

Received July 28, 1920.

It has generally been supposed that the devitrification of blown glassware in storage or in daily use is a phenomenon similar to that studied by Tammann,¹ Guertler² and others, which depends on the tendency of a supercooled liquid to form crystal nuclei, from which crystallization proceeds. Tammann showed that spontaneous devitrification depends on 2 factors, which seem to be related to the viscosity of the supercooled liquid: the tendency to form crystal nuclei, which increases with the degree of supercooling, though the rate at which nuclei have been observed to form reaches a maximum, and then on account of the damping effect of the diminishing temperature on the speed of formation, rapidly decreases and for most glasses reaches a value of zero at room temperature; and the speed with which crystallization proceeds from the crystal nucleus, which for commercial glassware also reaches a value of zero for ordinary temperatures. Tammann has shown that certain substances in solution act catalytically on the formation of crystal nuclei, and that in certain instances the rate may be depressed to zero even in the temperature range of the maximum. This is evidently the ideal condition for chemical glassware, a condition more or less successfully achieved by glass manufacturers.

It has also been shown³ that by repeated fusion and solidification supercooled liquids which otherwise devitrify readily can be obtained in the vitreous state. In all cases of this sort that have been studied water

¹ Tammann, *Z. Elektrochem.*, **10**, 532 (1904).

² Guertler, *Z. anorg. Chem.*, **40**, 268 (1904).

³ See Herbert Jackson, *Chem. News*, **120**, 62 (1920).