

5. Indirect, but apparently indisputable, evidence indicates that the second stage of the reaction is catalyzed in direct proportion to the hydrogen-ion concentration in acid solutions. Since the rate is also very rapid in alkaline solutions it is very likely catalyzed by hydroxyl ions as well.

6. The mathematical expression for the rate of hydrolysis in acid solutions is, therefore, $\frac{dC}{dt} = K_1(M) - k_1(I)(H^+)(Cl^-) + K_2'(I)(H^+)$. A simpler, but less obviously rational form of this equation is $\frac{dC}{dt} = \frac{2k_1(M)}{1 + k_3(Cl^-)} = \frac{0.304(M)}{1 + 6.14(Cl^-)}$. This equation has been found to hold with satisfactory accuracy for a wide variety of acid solutions.

7. The solubility of mustard gas in water at 25° is 0.0043 mole per liter. Substituting this value in the above equations gives the rate of hydrolysis in solutions saturated with mustard gas.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY]

THE ABSORPTION OF CARBON MONOXIDE BY CUPROUS AMMONIUM CARBONATE AND FORMATE SOLUTIONS

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Introduction

When hydrogen is made by the interaction of carbon monoxide and steam in the presence of a catalyst there is usually about 2-4% of carbon monoxide remaining in the gas produced. If this hydrogen is to be used in the synthesis of ammonia, a fairly complete removal of the carbon monoxide becomes necessary, since all ammonia catalysts so far suggested suffer a loss in efficiency if this gas is present. Thus, at low temperatures the loss due to 0.1% of carbon monoxide may become as much as 60-70% of the conversion of pure gas. This effect becomes very much less at higher temperatures but, unfortunately, the percentage of ammonia produced decreases rapidly as the temperature is raised. It is of importance, therefore, to operate at as low a temperature as possible, which means that the nitrogen-hydrogen mixture should be quite free from such catalyst poisons as carbon monoxide.

In practice the last traces of carbon monoxide are usually removed by passing the gas under pressure through ammoniacal copper solutions. At low temperatures it forms with cuprous solutions complex or possibly addition compounds which are readily decomposed when the temperature of the solution is raised. These solutions may therefore be regenerated by

heating them sufficiently to expel the absorbed gas. In the Synthetic Ammonia Process, solutions of cuprous ammonium carbonate and cuprous ammonium formate are known to present advantages over other copper solutions. The object of this investigation was to study the effectiveness of these two solutions.

Preparation of Solution

The solution of cuprous ammonium carbonate was prepared by dissolving ammonium carbonate in aqueous ammonia and adding cuprous oxide. Having fixed upon the concentration of copper and excess ammonia for a given solution, the weights of materials required were determined by assuming that $\text{Cu}_2(\text{NH}_3)_4\text{CO}_3$ represented the formula of the complex. In this calculation it must be remembered that $1/2$ of the ammonia in the complex is supplied by the ammonium carbonate.

In practice the solution was prepared as follows. The ammonium carbonate was dissolved in the ammonia and sufficient water added to give the necessary dilution. This solution was poured into a separatory funnel, cuprous oxide added, and a layer of light petroleum poured over the surface of the solution to exclude oxidation of the cuprous copper. The mixture was then warmed by immersing the funnel in water at about 50° at which temperature the copper oxide rapidly dissolved. A small amount of sediment which invariably appeared was removed by opening the stopcock and allowing some of the liquid to run out. The clear solution was then dropped into a 250cc. flask through which a stream of pure nitrogen was passing. A stream of pure carbon monoxide was then bubbled through the solution and the temperature subsequently raised to $60\text{--}70^\circ$. It soon became "water white" due to reduction of cupric copper by carbon monoxide. The excess of this gas was removed by bubbling nitrogen through the solution. The temperature was now lowered to that of the room when a faint blue color reappeared as a consequence of the exothermal reaction, $2\text{Cu}^+ \longrightarrow \text{Cu}^{++} + \text{Cu}$.

Reducing cupric copper by carbon monoxide gave a solution more nearly comparable with solutions used in technical operation where they are alternately cooled and warmed in an excess of carbon monoxide. This treatment was also desirable because it simplified analysis. In a "water white" solution it is safe to assume that the total copper is in the form of cuprous copper. This treatment was further desirable because loss of carbon monoxide by oxidation by the cupric copper was obviated, thereby simplifying the interpretation of the data.

The method of preparing the cuprous ammonium formate solution was essentially the same as that just described for the carbonate.

Preparation of Carbon Monoxide

The carbon monoxide used in these experiments was made by dehydrating formic acid by means of conc. sulfuric acid. The gas was purified and stored by the aid of the absorption apparatus A shown at the left in Fig. 1. The jacketed bulb contained cuprous ammonium formate solution, the temperature of which was fixed by that of the water in the surrounding jacket. The formate solution was saturated at a low temperature (about 15°) with carbon monoxide. Undissolved gases were completely expelled by opening the stopcock above the solution and lifting the mercury leveling bulb until the liquid was forced up into the cock. The dissolved carbon monoxide was now driven from the solution by passing warm water through the jacket. The gas was passed into the pipet B containing conc. sulfuric acid, which served to dry the gas and to remove the ammonia carried over from the formate solution. The carbon monoxide was stored over mercury in pipet E, from which it could be withdrawn as required for the absorption tests.

Apparatus and Experimental Method

The complete apparatus used in the experiments is shown in Fig. 1. Into the absorption pipet D, which was contained in a thermostat, known quantities of carbon monoxide could be admitted by means of the constant volume pipet C. Measured quantities of solution (10 cc. in all cases) were introduced by means of the solution pipet F.

The procedure followed was to evacuate the apparatus through S as far as the cocks C' and F'. The cocks C'' and S were then closed and the leveling bulb L' raised until the mercury level stood above C''. Ammoniacal copper solution was then drawn into the calibrated pipet F by lowering the mercury level in it and opening F', at the same time feeding in nitrogen to the supply flask. This solution was then sucked up into the evacuated absorption pipet D, together with enough mercury to fill the capillary tube below it. The vapor pressure of the solution at the selected absorption tempera-

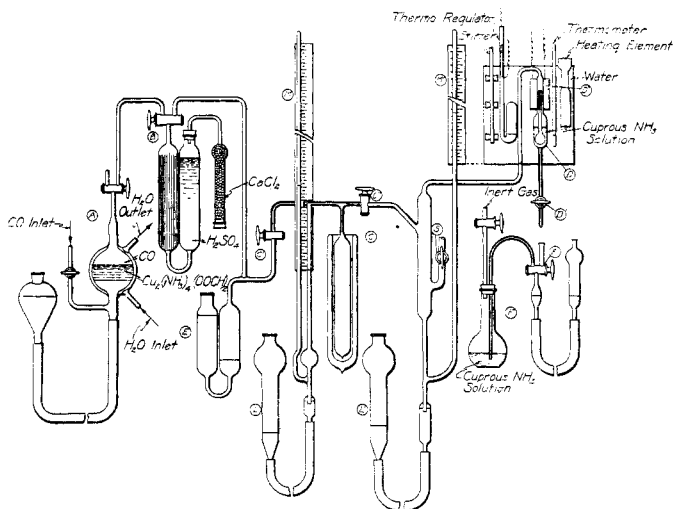


FIG. 1.

tures was then measured on the manometer M'. Carbon monoxide was now admitted to the pipet C, and its quantity determined by reading the manometer M; L' was then lowered to bring the mercury level slightly below C'', and carbon monoxide was bubbled into the absorption pipet, the amount being controlled by following the pressure change on the manometer M. The magnetically actuated stirrer in the absorption pipet was then brought into operation, and the absorption of carbon monoxide was followed by reading on the manometer M', the height of mercury column necessary to bring the mercury level to a fixed point on the stem of the absorption pipet. Even at the lowest temperature used (0°), the equilibrium pressure of carbon monoxide was attained within a few minutes.

Results

Absorption measurements were made at 0°, 20°, 40° and 60°. In Table I is given the composition, expressed in moles per liter, of the different solutions investigated. The table gives the vapor pressure of each of the solutions for those temperatures at which the solutions were studied. In

the last column of the table is given the amount of free copper which was deposited during the experiment.

TABLE I

Expt.	Composition; equivalents per liter				Vapor pressure; mm. of original solution				Cu pptd. G.
	Cu	CO ₂	HCOOH	NH ₃	0°	20°	40°	60°	
I	0.76	3.80	...	8.54	34	98	0.03
V	0.61	3.18	...	6.65	217	509	0.10
VI	0.77	3.08	...	6.94	204	472	0.26
II	0.84	...	3.04	6.52	24	76	215	517	0
III	0.94	...	3.20	7.17	26.5	91	274	687	0
IV	0.99	...	3.20	5.87	12	36	101	...	0.17
VII	0.61	...	2.92	6.43	249	605	0 0
VIII	0.80	...	2.85	6.62	180	426	0.0
X	0.80	...	1.37	4.47	15	317	...
IX	2.03	...	3.62	6.85	11

The observations made during Expt. II are given in Table II and are typical of all the results obtained. The results of the other experiments can

TABLE II

EQUILIBRIUM VALUES, EXPERIMENT II

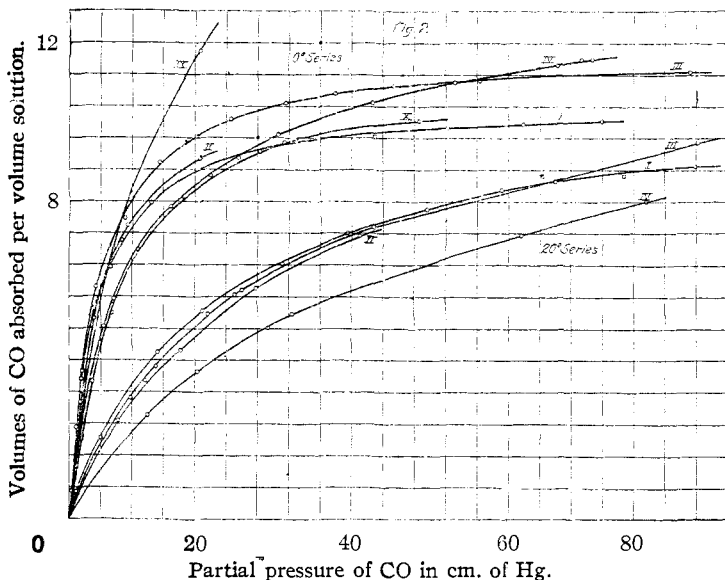
Pressure Mm. CO	Vols. of CO abs. per vol. soln.		Pressure Mm. CO	Vols. of CO abs. per vol. soln.	
	At 0°			At 40°	
...
12	...	4.59	64	...	1.17
33	...	8.29	128	...	1.91
73	...	11.56	...	At 60°	...
166	...	14.20
...	At 20°	...	185	...	0.90
...	331	...	1.49
62	...	3.85
141	...	6.67
239	...	9.08
369	...	11.10

be obtained from the curves given in Figs. 2 and 3. The results at 0° and 20° have been plotted separately from those at 40° and 60°, the former temperatures, particularly 0°, being considered absorption temperatures, while the latter are more properly regenerative temperatures. In all the observations made the volume of carbon monoxide absorbed was calculated for 0° and 760 mm. pressure. In deducting the vapor pressure of the solution it was assumed that this vapor pressure was independent of the carbon monoxide dissolved. This may not be strictly true, yet it probably did not introduce any considerable error in the results.

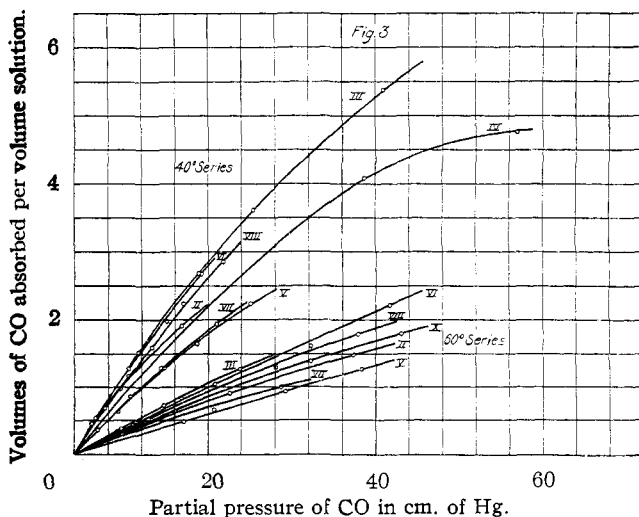
Discussion of Results

In the technical use of cuprous solutions for carbon monoxide removal we are interested in their absorptive powers at low temperatures and their

stability at temperatures sufficiently elevated to remove the carbon monoxide. Aside from the temperature effect, three factors appear to influence absorption, namely, cuprous concentration, ammonia concentration, and carbon monoxide concentration. Within the limits studied no effect was



noticed which might be traceable to the variations in concentration of total ammonium carbonate or formate. Because of the rapid decomposition



of the ammonium carbonate at higher temperatures it was necessary to keep its concentration in very great excess. In order, therefore, to make the

tests on formate solutions directly comparable with the carbonate solutions, the ammonium formate in these experiments was considerably in excess of that which might otherwise have been required. That the absorptive capacity of the formate solutions is not materially affected by the concentration of the excess ammonium formate may be seen by comparing the results of Expts. II and X. The slight discrepancies may be accounted for by the difference in the ammonia content of the two solutions. In all probability the absorptive capacity of the carbonate solutions would also have been found practically independent of the excess of ammonium carbonate. Therefore, in discussing the effect of composition only three variables will be considered, namely, copper, ammonia and carbon monoxide.

Our work has led us to the same conclusion arrived at by Hainsworth and Titus¹ regarding complex formation with carbon monoxide, namely, an unstable compound is probably formed containing 1 mole of the gas for each gram atom of cuprous copper. In other words, the absorption of carbon monoxide is proportional to the concentration of cuprous copper in the solution. This is shown by the fact that at low temperatures the absorption curves first show a rapid increase in the solubility of carbon monoxide with increasing pressure of this gas and then tend to become asymptotic to a line corresponding to 1 mole of carbon monoxide absorbed for each gram atom of cuprous copper. This complex molecule or addition compound is similar no doubt to that formed in the case of cuprous chloride, namely, $(\text{CuCl})_2 \cdot 2\text{CO}$. However, the exact nature of this complex is not known. Indeed, it is quite probable that there are a number of complexes present in equilibrium with each other, the relative amounts depending on the temperature and pressure.

If the absorption of carbon monoxide is proportional to the copper concentration it would seem advantageous to increase the cuprous copper content to the highest possible point. The very high absorptive power of the solution used in Expt. IX, as compared with that of Expt. X, shows that the solubility is almost doubled by doubling the copper content. Unfortunately, however, carbon monoxide reduces cuprous compounds quite appreciably as the concentration of copper is increased. From Table I, (see Expts. IV, V, VI) it will be seen that high copper content is accompanied by an increased precipitation of copper, the deposition being much more pronounced in the case of the carbonate solutions. In other words, the concentration of copper cannot be much in excess of 5.5% if considerable deposition of copper is to be avoided.

If the solution contains an equilibrium mixture of copper complexes it is quite likely that the absorptive capacity of each type of complex is not the same. Since the ammonia concentration undoubtedly determines

¹ Hainsworth and Titus, *THIS JOURNAL*, **43**, 1 (1921).

the nature of this equilibrium mixture, it would not be safe to predict the effect of ammonia on the absorption of carbon monoxide. Experimentally, however, we find for low pressures of carbon monoxide that its partial pressure decreases as the concentration of the ammonia is increased. Therefore, for very complete removal of carbon monoxide it is desirable to increase the free ammonia content as much as possible. The maximum concentration which might be used technically will depend, of course, upon the scheme employed for regeneration of the solutions. If the loss of ammonia during regeneration be kept low, 6-7% excess would be advantageous. Since the effectiveness of these solutions in the removal of carbon monoxide depends so much upon the way in which the absorption tower is operated, it is not safe to make any statement about the completeness with which the carbon monoxide may be removed in practice. But as far as our equilibrium measurements are concerned, it is quite evident that high ammonia pressure is necessary when fairly complete removal of carbon monoxide is desired.

Effects of Temperature

Stability.—Both the carbonate and the formate solutions were found to be stable at 0°. Copper, however, began to precipitate at higher temperatures when carbon monoxide was present. The reaction involved in the case of the carbonate solution probably follows the expression, $\text{Cu}_2(\text{NH}_3)_4\text{CO}_3 + \text{CO} + 2\text{H}_2\text{O} \rightarrow 2(\text{NH}_4)_2\text{CO}_3 + 2\text{Cu}$. That such a reaction does occur was demonstrated in the case of formate solutions which, after being exposed to carbon monoxide, showed on analysis the presence of carbonate. The extent to which this reaction occurred was found to increase with the temperature and to be much greater in the carbonate solutions than in the formate solution.

From the partial pressures of the solutions given in Table I, it will be observed that an undue amount of ammonia would be lost at 60° if the pressure over the solution were released.

Absorptive Power.—The curves all show that the absorptive power continually falls off as the temperature of the solution is increased. For any given concentrations of copper and ammonia, there appears to be no difference in the relative absorptive power between carbonate and formate solutions at any temperature.

At 0° the curves show a rapid increase in the solubility of carbon monoxide with increase in its partial pressure up to a point where the absorption capacity of a given solution has been nearly reached (approximately 1 mole of carbon monoxide per gram atom of copper). Here the slope changes rapidly and the absorption tends to become a linear function of the partial pressure—doubtless a simple solubility effect agreeing with Henry's law. At 60° the curves are more nearly straight lines, presumably owing to a greatly decreased tendency to form the complex.

From a comparison of Curves III and IV, it appears as if high ammonia concentration were also favorable in increasing the absorptive power of these solutions. The effect of copper concentration is, however, the important one.

Rate of Absorption.—The time necessary for the establishment of equilibrium was the same for both the carbonate and the formate, as nearly as we could observe. It seemed to depend primarily on the fresh surface exposed, and only secondarily on temperature changes, although as one would expect, the time necessary did decrease with increasing temperature. Since equilibrium in our experiments was reached in many cases in 2 to 3 minutes at 0° , with larger surfaces exposed we might expect equilibrium to be reached almost instantaneously.

Summary

1. A static method for studying the absorption capacity of liquid absorbents for carbon monoxide has been described, and the results of solubility tests on 3 cuprous ammonium carbonate and 7 cuprous ammonium formate solutions have been given.

2. It has been shown that for equivalent concentrations, the formate and carbonate solutions have essentially the same absorption capacity under the same conditions of temperature and partial pressure of carbon monoxide. At low temperatures (0°) the results indicate the formation of a complex or addition compound containing 1 mole of carbon monoxide per mole of copper, which is largely broken up at slightly elevated temperatures (60°). The experiments indicate that small variations in the concentration of total carbonate or formate have no appreciable effect on the solubility of carbon monoxide. It has been shown that the absorption of this gas is proportional to the copper concentration of the solution.

3. The carbonate solutions are very much less stable than the formate solutions, the former depositing copper rapidly at 60° . The maximum permissible copper concentration of any solution will be fixed by the temperature at which the solution is to be regenerated. High copper concentration is accompanied by increased precipitation of free copper as the temperature is raised. High pressures of carbon monoxide also tend to increase the precipitation of copper.

4. The experiments show that cuprous ammonium formate solutions are preferable to carbonate solutions because the deposition of copper at regeneration temperatures is very much less.

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