Studies on the Ammoniacal Copper Solutions I
The Reaction Order of the Reduction by Carbon Monoxide and a Correction for the Escaping Carbon Monoxide

By Minoru HIRATA

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It is a well-known fact that ammoniacal solutions of cuprous compounds absorb readily carbon monoxide.(1) Such solutions are used in determining carbon monoxide in gas analysis and for the purification of material gases in the ammonia manufacturing industry to remove carbon monoxide.

For the latter purpose, solutions containing both cuprous and cupric compounds are used circulating. In this case the absorbed carbon monoxide reduces cupric compounds in copper solutions and prevents the solutions from the increase of cupric compounds content which would be caused by the oxygen in material gases.

Hainsworth and Titus,(2) Larson and Teithworth,(3) Gump and Ernst(4) and Möller(5) studied on those solutions, but in spite of the importance of the reducing action of carbon monoxide the kinetics of the reduction were hitherto scarcely investigated. The present author has aimed to make clear this problem.

The compositions of the original copper solutions employed in the studies are shown in Table 1.

Table 1 (g./100 cc.)

Cu^I	Cu^{II}	NH_3	HCOOH	CO_2
8–15	1–5	8–16	2–10	6–13

Theoretical

It is verified that two mols of cupric copper are reduced by one mol of carbon monoxide and at the same time produce one mol of carbon dioxide. Though it is difficult to show the actual details of the reaction definitely, these experimental facts may be expressed by the following scheme,

$$2\,Cu^{II} + CO \longrightarrow 2\,Cu^{I} + CO_2 \qquad (1)$$

Here, Cu^{II} and Cu^{I} express the cupric and cuprous compounds respectively, whose chemical formulas have not yet been definitely determined.

According to the author's experiments, the reaction velocity of the reduction is proportional to each concentration of cupric copper and the absorbed carbon monoxide. Hence remembering the stoichiometric relation expressed by (1), it may be considered that the reduction occurs in two stages; the reaction of the first stage (2) which proceeds far slowly in comparison with the second stage (3) decides consequently the reduction velocity.

$$Cu^{II} + CO \longrightarrow Cu^{I} + CO^{*} \qquad (2)$$

$$Cu^{II} + CO^{*} \longrightarrow Cu^{I} + CO_2 \qquad (3)$$

The author assumed that in the reaction of the first stage carbon monoxide is converted into an unstable intermediate state which has lost a half of its reducing power and this substance causes immediately the further reduction in the second stage. Though the nature of the intermediate state of carbon monoxide is not clear, it should correspond electronically to CO^+ and so is described by CO^* in the present paper. The results of reactions (2) and (3) coincide stoichiometrically with that of the reaction (1).

Let the initial concentrations of Cu^{II} and carbon monoxide be represented by a and b respectively, and let the concentration increase of Cu^I after time θ by x. The following two expressions may be given for the reduction velocity according to the above-mentioned reduction mechanism (1), and (2) and (3) respectively,

$$\frac{dx}{d\theta} = k^{III}(a-x)^2\left(b-\frac{x}{2}\right) \qquad (4)$$

and

$$\frac{dx}{d\theta} = k\,(a-x)\left(b-\frac{x}{2}\right), \qquad (5)$$

where k^{III} and k are the velocity constants respectively.

From the author's experiments, it has been known that k is nearly constant independently of the lapse of time, while k^{III} increases with it. Namely the reduction is of the second order.

In almost all of actual reactions, some of the absorbed carbon monoxide escape unreacted from solutions, therefore in such cases equation (5) should be corrected as follows,

$$\frac{dx}{d\theta} = k(a-x)\left(b-\frac{x}{2}-v\right), \qquad (6)$$

where v is the concentration of the escaped carbon monoxide during the time θ.

If it is assumed that the escaping velocity of the gas is proportional to its average concentration in the solution at that time,

$$\frac{dv}{d\theta} = k'\left(b-\frac{x}{2}-v\right) \qquad (7)$$

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(1) Condamine, *Compt. rend.*, **179**, 691 (1925); Moser u. Hanika, *Z. anal. Chem.*, **67**, 448 (1926); D. R. P., 289694 (1914)

(2) *J. Am. Chem. Soc.*, **43**, 1 (1921)

(3) *J. Am. Chem. Soc.*, **44**, 2878 (1922)

(4) *Ind. Eng. Chem.*, **22**, 382 (1930)

(5) *Z. anorg. allgem. Chem.*, **224**, 113 (1935); ibid., **224**, 130 (1935)

is obtained, where k' is a constant characteristic of the reduction which we name the "exhalation coefficient".

When $b-\frac{x}{2} \gg v$, equation (7) should be strictly true.

From equations (6) and (7),

$$\frac{dv}{dx}=\frac{k'}{k}\cdot\frac{1}{a-x} \tag{8}$$

is obtained. Integrating equation (8),

$$v=-\frac{k'}{k}\ln(a-x)+\beta_1 \tag{9}$$

is obtained, where β_1 is an integration constant. At the initial state, $x=0$ and $v=0$, therefore,

$$\beta_1=\frac{k'}{k}\ln a \tag{10}$$

Inserting equation (10) into (9),

$$v=\frac{k'}{k}\ln\frac{a}{a-x} \tag{11}$$

If the value of v corresponding to any value of $a-x$ is known, that of $\frac{k'}{k}$ can be found out. Consequently the value of v against any arbitrary value of $a-x$ can be calculated.

By raising the temperature after the reduction is almost finished, the value of $a-x$ at the practical completion of reduction $(a-x)_{\theta=\infty}$ is obtaind. On the other hand, the value of v at that time $v_{\theta=\infty}$ is found out as the difference between the quantity of the carbon monoxide initially absorbed and the quantity expended in the reduction.

Then, from equation (11),

$$\frac{k'}{k}=\frac{v_{\theta=\infty}}{\ln\frac{a}{(a-x)_{\theta=\infty}}} \tag{12}$$

is obtained.

From equations (11) and (12), v is written as follows:

$$v=\frac{v_{\theta=\infty}}{\ln\frac{a}{(a-x)_{\theta=\infty}}}\ln\frac{a}{a-x} \tag{13}$$

In practical calculation, the cupric copper concentration $a-x$ with the lapse of time θ was observed, from which the $(a-x)$——θ curve was plotted. This curve was utilized for correcting the value of $a-x$ against θ, and this was necessary on account of the instability of copper solution.

Practically, velocity constants were numerically calculated instead of integrating equations (4), (5) or (6); for instance, equation (14) was adopted instead of equation (6),

$$\frac{x_i-x_{i-1}}{\theta_i-\theta_{i-1}}=\frac{1}{2}k\left(a-\frac{x_i+x_{i-1}}{2}\right)\left(2b-\frac{x_i+x_{i-1}}{2}-2v_i\right) \tag{14}$$

$i-1$ and i mean the successive numbers of measurements, and v_i is the value expressed by equation (15),

$$v_i=\frac{k'}{k}\ln\frac{a}{\left(a-\frac{x_i+x_{i-1}}{2}\right)} \tag{15}$$

Experimental

Experiments were made as follows; 70.0 cc. of copper solution was taken, and it was allowed to absorb a certain quantity of carbon monoxide. Then this solution was portioned 5.00 cc. each into several test tubes. The surface of the copper solution was always covered with liquid paraffin to prevent the evaporation of the solution, the loss of ammonia and carbon dioxide by escaping, and the oxidation of cuprous compounds by air.

The test tubes were dipped into a thermostat of the accuracy of ± 0.1°C, and the change of the cupric copper concentrations with the time elapsed was observed. It required 3 to 5 minutes for the contents of the test tubes to reach a certain temperature after dipping into the bath. At the end of the experiment, the last test tube was dipped into a water bath of 75°C for the period of 30 minutes to complete the reduction. In most cases, reduction was practically completed before the latter treatment was carried out. It was confirmed that the evaporation and the loss of copper solution and its spontaneous oxidation by diffusion of air would scarcely take place throughout the experiment.

The order of the reaction The two examples in which carbon monoxide scarcely escaped unreacted from the solutions are quoted in Tables 2 and 3. The small quantities of the escaped carbon monoxide were neglected, and k^{III} and k calculated using equations (4) and (5) are given.

Table 2 R. 61

No. of measurement i	Time θ_i min.	$\theta_i-\theta_{i-1}$ min.	Cu^{II}-conc. obs. g.mol/l.	Cu^{II}-conc. $a-x_i$ corr. g.mol/l.	x_i-x_{i-1} g.mol/l.	$\frac{x_i+x_{i-1}}{2}$ g.mol/l.	k^{III} g.mol/l. min.	k g.mol/l. min
0	0	—	0.508	0.508	—	—	—	—
1	5	5	0.453	0.453	0.055	0.028	(0.458)	(0.220)
2	10	5	0.423	0.419	0.034	0.072	0.439	0.190
3	15	5	0.388	0.393	0.026	0.102	0.470	0.191
4	20	5	0.374	0.374	0.019	0.125	0.467	0.179
5	30	10	0.345	0.345	0.029	0.149	0.516	0.181
6	50	20	0.310	0.310	0.035	0.181	0.595	0.195
7	90	40	0.280	0.280	0.030	0.213	0.750	0.221
8	150	60	0.275	0.275	—	—	—	—
9	300	150	0.275	0.275	—	—	—	—
10	∞	—	0.275	0.275	—	—	—	—

Initial concentration of CO : 0.1181 g.mol/l.
Reaction rate of CO : 98.7% Temperature of experiment : 50.0°C

Table 3 R. 64

No. of measurement i	Time θ_i min.	$\theta_i-\theta_{i-1}$ min.	Cu^{II}-conc. obs. g.mol/l.	Cu^{II}-conc. $a-x_i$ corr. g mol/l.	x_i-x_{i-1} g.mol/l.	$\frac{x_i+x_{i-1}}{2}$ g mol/.	k^{III} g mol/l. min.	k g.mol/l. min.
0	0	—	0.512	0.512	—	—	—	—
1	5	5	0.462	0.462	0.050	0.025	(0.391)	(0.190)
2	10	5	0.434	0.429	0.033	0.067	0.383	0.170
3	15	5	0.404	0.403	0.026	0.096	0.414	0.172
4	20	5	0.379	0.382	0.021	0.120	0.452	0.177
5	30	10	0.349	0.352	0.030	0.145	0.464	0.170
6	50	20	0.316	0.316	0.036	0.178	0.512	0.171
7	90	40	0.287	0.287	0.029	0.211	0.552	0.161
8	150	60	0.275	0.275	—	—	—	—
9	300	150	0.275	0.275	—	—	—	—
10	∞	—	0.275	0.275	—	—	—	—

Initial concentration of CO : 0.1204 g.mol/l.
Reaction rate of CO : 98.5%
Temperature of experiment : 50.0°C

Now it is clear from the tables that k is constant independently of the time elapsed, while k^{III} increases with it and so the reducing reactions are of the second order.

The correction for the escaping carbon monoxide The results of the experiments where the escaping of carbon monoxide seemed pretty high, are given in Tables 5 and 6. In the last columns k calculated from equation (14) are tabulated. We can see that k calculated in such a way is constant enough through the whole course of each experiment. The compositions of the copper solutions used in the experiments are shown in Table 4.

Table 4

No. of experiment	Total Cu g.mol/l.	NH_3 g.mol/l.	HCOOH g.mol/l.	CO_2 g.mol/l.
R. 20	1.02	5.12	0.36	1.60
R. 70	0.30	1.04	0.10	0.31

Table 5 R. 20

No. of measurement i	Time θ_i min.	$\theta_i-\theta_{i-1}$ min.	Cu^{II}-conc. obs. g.mol/l.	Cu^{II}-conc. $a-x_i$ corr. g.mol/l.	$2v_i$ g.mol/l.	x_i-x_{i-1} g.mol/l.	$\frac{x_i+x_{i-1}}{2}$ g.mol/l.	k
0	0	—	0.463	0.463	0	—	—	—
1	2	2	0.448	0.448	0.001	0.015	0.008	(0.193)
2	5	3	0.443	0.439	0.002	0.009	0.020	0.0858
3	8	3	0.432	0.431	0.002	0.008	0.028	0.0818
4	13	5	0.421	0.419	0.003	0.012	0.038	0.0812
5	20	7	0.407	0.405	0.004	0.014	0.051	0.0777
6	30	10	0.387	0.388	0.006	0.017	0.067	0.0803
7	50	20	0.366	0.362	0.008	0.026	0.088	0.0846
8	90	40	0.330	0.330	0.011	0.032	0.117	0.0889
9	150	60	0.310	0.310	0.014	0.020	0.143	(0.0907)
10	300	150	0.305	0.305	—	—	—	—
11	∞	—	0.300	0.300	0.017	—	—	—

Initial concentration of CO : 0.0898 g.mol/l.
Reaction rate of CO : 90.8%
Temperature of experiment : 50.0°C

Table 6. R 70

No. of measurement i	Time θ_i min.	$\theta_i-\theta_{i-1}$ min.	Cu^{II}-conc. obs. g.mol/l.	Cu^{II}-conc. $a-x_i$ corr. g.mol/l.	$2v_i$ g.mol/l.	x_i-x_{i-1} g.mol/l.	$\frac{x_i+x_{i-1}}{2}$ g.mol/l.	k
0	0	—	0.102	0.102	0	—	—	—
1	5	5	0.093	0.093	0.001	0.009	0.005	(1.032)
2	10	5	0.086	0.087	0.003	0.006	0.012	0.987
3	15	5	0.083	0.083	0.004	0.004	0.017	0.896
4	20	5	0.077	0.080	0.005	0.003	0.021	0.924
5	30	10	0.077	0.076	0.006	0.0045	0.024	0.962
6	50	20	0.072	0.071	0.007	0.0045	0.029	(1.027)
7	90	40	0.068	0.068	—	—	—	—
8	150	60	0.068	0.068	—	—	—	—
9	300	150	0.077	0.068	—	—	—	—
10	∞	—	0.077	0.068	0.008	—	—	—

Initial concentration of CO : 0.0212 g.mol/l.
Reaction rate of CO : 80.3%
Temperature of experiment : 50.0°C

These facts seem to prove the above-mentioned assumption, equation (7), which was made for the calculation to correct the effect of the escaping carbon monoxide to be quite appropriate.

Summary

1. It is experimentally verified that the reduction of cupric copper by the carbon monoxide absorbed in the copper solution is a reaction of the second order.

2. In the calculation of the velocity constant for the reduction, it is found that the correction made for the carbon monoxide escaping unreacted, under the assumption that the escaping velocity of the carbon monoxide is proportional to its concentration in the solution at that time, is appropriate.

Research Department, Niihama Works,
Nissin Chemical Co., Ltd.