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STORRS, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF TORONTO]

Rates of Copper Dissolution in Aqueous Ammonium Hydroxide Solutions[1]

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The rates of dissolution of polycrystalline metallic copper in aqueous ammonium hydroxide solutions have been determined under various experimental conditions. Over a considerable range of conditions the dissolution has been found to be autocatalytic. The autocatalytic dissolution is well represented by a half-order rate equation. An empirical equation is presented which represents the autocatalytic rate data with an average deviation of ±4%. The rate equation is discussed in terms of a mechanism which assumes that the rate controlling process is the removal of cuprous ion species from the copper solution interface by diffusion. Data are also given for an essentially zero-order rate of dissolution observed when the dissolving medium was concentrated with respect to oxygen or very dilute with respect to cupric ion species.

Introduction

There have been four previous investigations of the dissolution of copper in aqueous ammonia solutions.[2-5]

The earliest work by Yamasaki[2] was done using air-saturated solutions. Evidence was found for autocatalysis and for an initial rate which was independent of ammonia concentration. Lane and McDonald[3] more recently investigated the dissolution of copper in oxygen-saturated ammonia solutions. Under these quite different experimental conditions they found no evidence for autocatalysis and reported a first-order dependence on ammonia concentration. Rather surprisingly, they stated that their results seemed to disprove the conclusions of Yamasaki. The data of these two early contributions are considered by Halpern[5] to be discrepant and to provide conflicting information. Halpern reported data for the corrosion of copper in aqueous ammonia solutions saturated with oxygen at pressures up to about eight atmospheres. He found no evidence for autocatalysis and reported a first order dependence on [NH_3] and [NH_4^+].

It is apparent that the experimental conditions and the data given by Halpern are similar to those reported by Lane and McDonald. It is also evident that the experimental conditions and the data reported by Yamasaki are very different from those reported in the two later contributions. It would seem reasonable to consider the possibility that no conflict or inconsistency exists, but rather that all the data are valid for the conditions specified.

Experimental

The apparatus used was essentially the same as previously described.[6] It consisted of a covered Pyrex beaker in which a cylinder of copper was rotated. The copper cylinder (1.8 cm. diameter) was rotated by means of an axially mounted lucite rod. The ends of the copper cylinder were protected from the corroding medium by lucite washers. The solution in the beaker was kept saturated with air or oxygen by bubbling the appropriate gas through the solution. The gas was passed through one wash bottle containing dilute sodium hydroxide solution and two containing ammonium hydroxide solution before introduction into the dissolving medium. The copper samples used in this work were machined from refinery copper rod (99.95 +% copper) which was supplied by the Anaconda American Brass Ltd. The samples were polished with 3/0 emery paper. Rate determinations were done by solution analysis. Samples of the copper solution were withdrawn periodically, evaporated to dryness, made up with dilute hydrochloric acid and the copper content was determined polarographically.

Results and Discussion

Rate Dependence on Copper Concentration.—The primary point to be established is whether the dissolution of copper in aqueous ammonium hydroxide solutions is or is not an autocatalytic reaction. As shown in Fig. 1 we have found an essentially zero-order rate for the dissolution of copper in 0.76 N aqueous ammonium hydroxide solution saturated with oxygen at one atmosphere. Thus under these conditions there is little evidence for autocatalysis. This conclusion agrees with those of Lane and McDonald and of Halpern who used oxygen-saturated solutions. However, the data which we have obtained for the dissolution in air-saturated ammonium hydroxide solutions, Fig. 2, are convincing evidence for the existence of an autocatalytic reaction under conditions similar to those employed by Yamasaki. Thus we find no conflict or discrepancy between the data of Yamasaki and those of Lane and McDonald. It is apparent that the mechanism of the dissolution is not the same for both sets of experimental conditions.

The major conclusions reached by Lane and McDonald for high oxygen pressure have been verified by Halpern. We have not extended the investigation of copper dissolution under these conditions. However, some additional work has been done on the dissolution of copper in air-saturated solutions under the conditions which result in an autocatalysis.

All the data which have been obtained in this Laboratory for the autocatalytic dissolution of copper have given linear half-order plots as shown in

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(1) This work was supported by The President's Advisory Committee on Scientific Research of the University of Toronto and by The Corrosion Subcommittee of the National Research Council, Ottawa.

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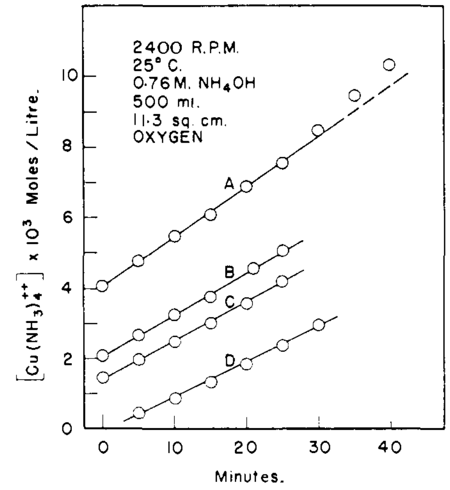

Fig. 1.—Dissolution of copper in oxygen-saturated ammonium hydroxide solutions. Copper was added initially to the solution used to obtain curves A, B and C in the form of $CuSO_4$ or $Cu(NH_3)_4(OH)_2$. The figures in the left-hand corner refer to the sample rotation speed, the temperature, the solution concentration, the volume of the corroding medium, the area of the copper sample and the gas in equilibrium with the corroding medium.

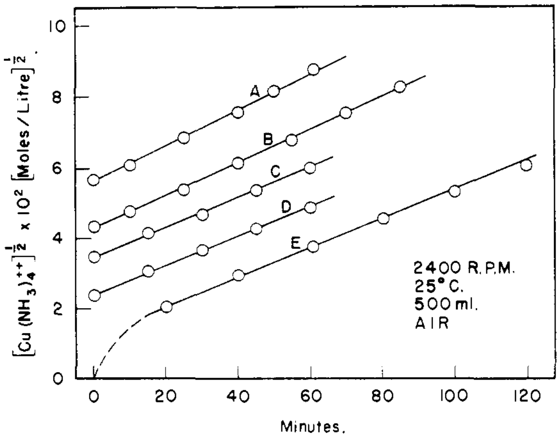

Fig. 2.—Dissolution of copper in air-saturated ammonium hydroxide solutions. Copper was added initially to the solution used to obtain curves A, B, C and D. Curve A, (NH_4OH), 1.52 *N*, copper specimen area 11.3 sq. cm.; curve B, 0.76 *N*, 11.4 sq. cm.; curve C, 0.38 *N*, 10.2 sq. cm.; curve D, 0.38 *N*, 10.2 sq. cm.; curve E, 0.38 *N*, 10.5 sq. cm.

Figs. 2, 3, 4 and 6. The data also give parallel half-order plots for various initial copper concentrations at a given ammonium hydroxide concentration. The rate is only slightly dependent on ammonium hydroxide concentration as shown in Fig. 2 and Table I.

TABLE I

THE EFFECT OF AMMONIUM HYDROXIDE CONCENTRATION

$[NH_4OH]$		$\frac{d[Cu(NH_3)_4^{++}]^{0.5}}{dt}$
0.38		4.30×10^{-4}
0.76		4.64×10^{-4}
1.52		4.65×10^{-4}
2400 r.p.m.		500 ml.
25°C.	Air	10.5 sq. cm.

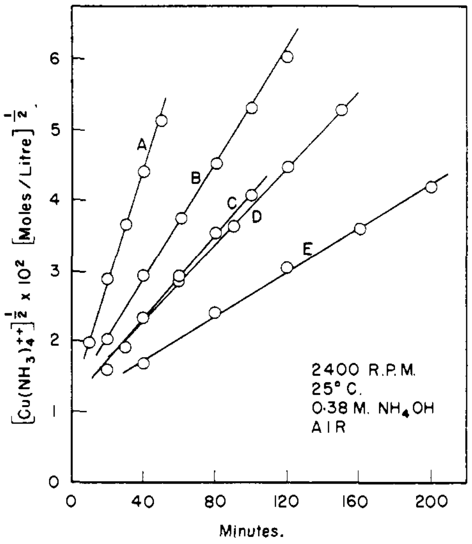

Fig. 3.—Effect of solution volume and surface area: A, solution volume 250 ml., copper specimen area 10.3 sq. cm.; B, 500 ml., 10.5 sq. cm.; C, 750 ml., 10.3 sq. cm.; D, 500 ml., 6.0 sq. cm.; E, 1500 ml., 11.3 sq. cm.

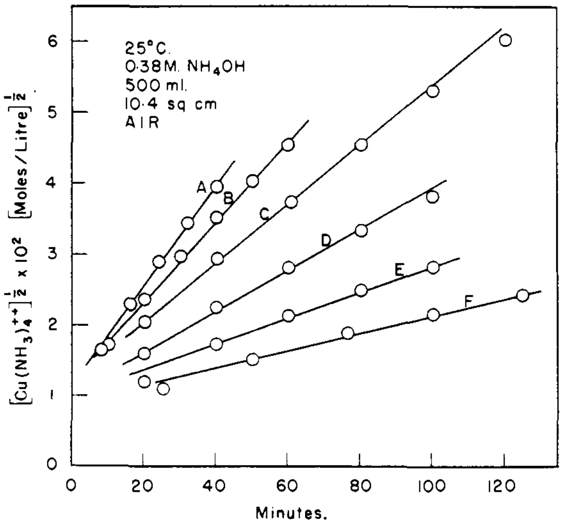

Fig. 4.—Effect of rotation speeds in r.p.m.; A, 4350; B, 3450; C, 2400; D, 1200; E, 600; F, 300.

Thus for the autocatalytic reaction we may write

$$\frac{d[Cu(NH_3)_4^{++}]}{dt} = K_1[Cu(NH_3)_4^{++}]^{1/2} \qquad (I)$$

where the formula $[Cu(NH_3)_4^{++}]$ for the predominant species is used to represent the total molar concentration of cupric ion species.

This rate dependence is consistent with the following assumptions.

(i) The concentration of cupric ion species in the bulk of the solution is assumed to be equal to the concentration of cupric ion species at the copper solution interface.

$$[Cu(NH_3)_4^{++}] = [Cu(NH_3)_4^{++}]_i$$

(ii) The cuprous ion, cupric ion equilibrium

$$Cu(NH_3)_4^{++} + Cu \rightleftharpoons 2Cu(NH_3)_2^{+}$$

is assumed to be established at the interface.

$$[Cu(NH_3)_2^{+}]_i = K_2[Cu(NH_3)_4^{++}]_i^{1/2}$$

(iii) The removal of cuprous ion species from the interface is assumed to be a first-order reaction.

$$-\frac{d[Cu(NH_3)_2{}^+]_i}{dt} = K_3[Cu(NH_3)_2{}^+]_i$$

The rate of increase of cupric-ion species in the bulk becomes

$$\begin{aligned}\frac{d[Cu(NH_3)_4{}^{++}]}{dt} &= K_3[Cu(NH_3)_2{}^+]_i \\ &= K_2K_3[Cu(NH_3)_4{}^{++}]_i{}^{1/2} \\ &= K_2K_3[Cu(NH_3)_4{}^{++}]^{1/2}\end{aligned}$$

On the basis of these assumptions the experimental half-order rate constant K_1 may be identified as K_2K_3.

Rate Dependence on Sample Area and Solution Volume.—The effect of variations of solution volume and sample area are shown in Fig. 3. The rate constant for the half-order equation is directly proportional to the sample surface area and inversely proportional to the volume of the corroding solution. This effect provides additional support for the autocatalytic rate equation.

Surface Roughness.—In order to eliminate the possibility that the rate data for the autocatalysis might be influenced by the increase in surface roughness during a run, rate data were obtained for samples of various initial surface roughness between 4.5 and 40.0 microinches. These rates were found to be identical and quite independent of surface roughness. It may be noted that surface roughness variations of this order were found during a typical run.

The data reported by Yamasaki[2] for the autocatalytic dissolution of copper in ammonium hydroxide solutions when replotted also gave linear half-order plots for the initial dissolution rate. Linear plots were obtained for dissolution times up to two hours for the more concentrated ammonium hydroxide solutions.

A similar rate equation has been reported[6] for the dissolution of copper in aqueous sulfuric acid solutions. In that case the rate constant was found to be independent of the rate of rotation of the sample. Hence, it was assumed that the cuprous ion removal from the interface was accomplished by a first-order chemical reaction rather than by a diffusional process.

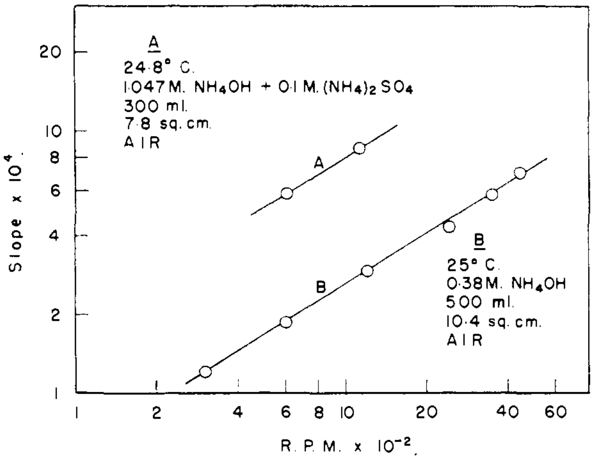

Fig. 5.—Rate of dissolution as a function of rotation speed: A, Yamasaki's data,[2] s, the slope, was obtained from the replot on half-order basis; B, our data, s, is the slope of plot from Fig. 4.

The Effect of Rotation Speed.—For the dissolution of copper in aqueous ammonium hydroxide solutions there is a considerable effect of rotation speed as shown in Fig. 4. Figure 5 illustrates that K_1 of equation I is proportional to r.p.m. to the 0.65 power. This power is somewhat less than the power 0.8 which is frequently accepted as the value for a simple diffusion process. However, it is at least an indication that diffusion control is a major factor in the dissolution.

These data confirm and extend the data of Yamasaki who found for two values of r.p.m. that the rate varied with r.p.m.$^{2/3}$.

Rate Dependence on Temperature.—The effect of temperature on the rate of dissolution is illus-

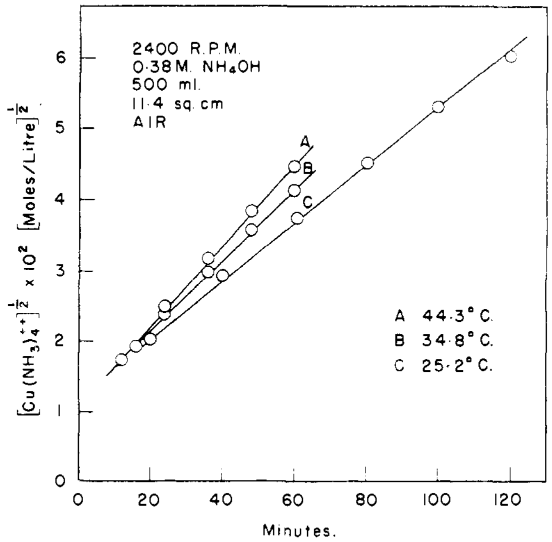

Fig. 6.—Effect of temperature in °C.: A, 44.3; B, 34.8; C, 25.2.

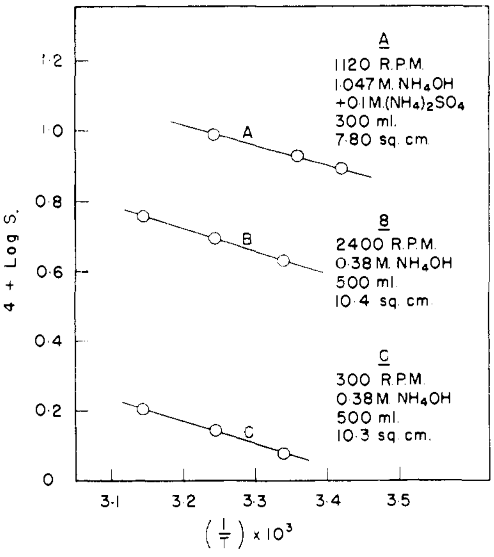

Fig. 7.—Rate of dissolution as a function of temperature: A, Yamasaki's data, s, the slope, was obtained from the replot on half-order basis.

trated by the data given in Fig. 6. The temperature variation corresponds to an apparent activation energy of 2.9 kcal. per mole as shown in Fig. 7. The apparent activation energies determined at 300 and 2400 r.p.m. were essentially the same. Because of the possible equilibrium involved it is doubtful that this value is the activation energy of the controlling reaction. Although the value is very low it cannot be regarded as unequivocal confirmation for a diffusional control.

Effect of Ammonium Hydroxide Concentration.—The data which have been obtained for the effect of ammonium hydroxide concentration are given in Table I.

At concentrations below 0.38 *M* the rate fell rapidly. Above this concentration the rate was almost independent of the ammonium hydroxide concentration. These data confirm the conclusions of Yamasaki who found little variation in initial rates of dissolution for ammonium hydroxide concentrations from 0.5 to 4.0 *M*.

Empirical Equation and Range of Application.—The data discussed above for the autocatalytic dissolution of copper in air-saturated ammonium hydroxide solutions may be summarized by the equation

$$\frac{d[Cu(NH_3)_4{}^{++}]}{dt} = 1.21 \times 10^{-5} \frac{A}{V} e^{-\frac{2920}{RT}} \bar{V}^{0.65} [Cu(NH_3)_4{}^{++}]^{0.5}$$

Ranges of Experimental Conditions

$[Cu(NH_3)_4{}^{++}]$	total concn. of cupric species 4–80 × 10^{-4} moles/l.
T	temperature 298–317°K.
A	sample area 6–11.4 sq. cm.
V	soln. vol. 0.25–1.5 l.
t	dissolution time 20–120 min.
$\bar{V}$	peripheral velocity 1700–24600 cm./min.
$[NH_4OH]$	0.38–1.52 moles/l.

The value 1.21 × 10^{-5} is an average for 30 plots. The average deviation from this value is ±0.043 × 10^{-5} or about 4%.

Some of the data presented by Yamasaki fall within the range of the empirical equation. Most of the information needed to evaluate the equation using Yamasaki's data for initial dissolution rates is available. However, Yamasaki used plate samples and the calculation of $\bar{V}$ is in doubt because of differences in flow patterns. Despite this uncertainty the value of the constant for the above equation using the data of Yamasaki is calculated to be 1.65 × 10^{-5}.

Although the data in Figs. 1 and 2 indicate that in general the reaction is half-order in air-saturated solutions and zero order in oxygen-saturated solutions, it must be noted that oxygen concentration alone is not sufficient criterion for autocatalytic control. In air-saturated solutions at very low copper concentrations the reaction is approximately zero order as may be seen from plot E of Fig. 2 and from Table II.

TABLE II

INITIAL DISSOLUTION OF COPPER IN AIR-SATURATED 0.38 *M* AMMONIUM HYDROXIDE SOLUTION

Time, min.	Copper concn., mole/l. × 10^4	$\frac{[Cu(NH_3)_4{}^{++}]}{t}$, mole/l./min. × 10^4
3	0.51	0.170
6	1.03	.172
9	1.64	.182
12	2.23	.186
15	2.85	.190

2400 r.p.m. 500 ml.
25°C. 10.2 sq. cm.

Alternatively in oxygen-saturated solutions at high cupric ion species concentration there is some evidence for incipient autocatalysis as shown by plot A of Fig. 1. Although the limits of the ranges of each mechanism are by no means clearly delineated there seems little doubt that the mechanism of the dissolution of copper in aqueous ammonium hydroxide solutions may change considerably with variations in experimental conditions. Within a limited range the reaction has been shown to be autocatalytic. The rate controlling process is assumed to be the removal of cuprous ion species from the metal solution interface by a diffusional operation.

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