1970

Kinetics of copper dissolution

Rogelio Andres Panlasigui

Iowa State University

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Kinetics of copper dissolution

by

Rogelio Andres Panlasigui

A Dissertation Submitted to the
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The Requirements for the Degree of
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Dean of Graduate College

Iowa State University
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1970
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INTRODUCTION

According to Grimston (15) the world consumption of the main metals grew over the seven-year period 1960-1967 at the following annual rates:

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<td>Aluminum</td>
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</tr>
<tr>
<td>Nickel</td>
<td>8</td>
</tr>
<tr>
<td>Steel</td>
<td>5 1/2</td>
</tr>
<tr>
<td>Zinc</td>
<td>5 1/2</td>
</tr>
<tr>
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These values include estimates for the communist countries. The consumption of all these metals has increased although substitution of non-metallic materials for metals and of one metal for another has also increased.

Copper has special properties that make it suitable for a wide range of applications. It has high thermal and electrical conductivity, excellent ductility, and resistance to corrosion. Thus, in a world of expanding electrification, growing population, and rising standards of living the demand for copper is great and continues to grow (29). The market for copper alloys has also expanded because of new technology. Weight savings in design has opened new applications for copper alloys such as central heating installations (25). A survey of materials used in water desalting plants indicates that copper alloys give the
best performance (7).

But as the demand for copper increases steadily, reserves are being constantly depleted and sources of decreasing copper content have to be utilized. In the United States, the recoverable content of the average ore has declined on the average by 5 percent annually since 1964. Thus in 1968 the recoverable copper content of the average ore declined from 0.63 to 0.60 percent (30). As the mining industry is confronted with low-grade copper-bearing ores and waste rock which cannot be processed economically by milling and concentrating, leaching methods become more attractive. The problem of air pollution also makes leaching appear more attractive than smelting (8). In the free world leaching has accounted for 150,000 tons or 3 percent of the 5,000,000 tons of primary copper produced annually in the mid-1960's. Production of copper by leaching is expected to increase fivefold by 1975 (6).

Investigations made on leaching various copper minerals have shown that several copper sulfide minerals are soluble to some extent in sulfuric acid solutions containing ferric sulfate and that many copper oxide minerals are soluble in ammoniacal solutions (26). The more extensively applied solvent is dilute sulfuric acid not only because it readily dissolves the metal but also renders it in a form more suitable for recovery. Sulfuric acid, however, has the disadvantage of dissolving carbonate, silicate, and oxide compounds in the
gangue which makes the dissolution inefficient. These impurities also tend to accumulate when the solution is recycled. Ammonia, unlike sulfuric acid, does not dissolve the gangue (10).

On a commercial scale the leaching of native copper ores by a solution of ammonia and ammonium carbonate is possible as in the case of Calumet and Hecla Mining Co. (3). Universal Mineral and Metals, Inc. leaches scrap copper by a solution of ammonia, ammonium carbonate, and copper ammonium carbonate (37). Perhaps, leaching copper oxide ores treated with a preliminary reducing roast is economically feasible.

Although leaching copper with ammonia is commercially applied, the nature of the reaction is not well understood. Several contradictions exist in the results of earlier investigations on the dissolution of metallic copper in aqueous ammonia. One basic difference was that on one hand Yamasaki (36), Vora (32), and Wu (35) observed that the dissolution rate of copper increased as the concentration of copper in solution increased while on the other hand Lane and McDonald (19) and Halpern (16) did not observe such autocatalytic effect. Lane and McDonald as well as Halpern also found that the dissolution rate of copper was first order with respect to ammonia. However, Yamasaki showed that the dissolution rate of copper was independent of ammonia concentration and that it was first order with respect to the copper concentration in solution and
half order with respect to the concentration of oxygen. The effect of adding an ammonium salt such as ammonium carbonate in solution was not clear. Yamasaki found that the rate of dissolution of copper was independent of the concentration of ammonium salt while Halpern observed that the dissolution rate was also first order with respect to the concentration of ammonium ion. Yamasaki speculated that the reaction might be diffusion controlled but he concluded otherwise while Lane and McDonald pointed out that the dissolution rate was partially diffusion controlled. Halpern observed that at low oxygen pressures the dissolution rate of copper was determined by the transport of oxygen to the reaction surface.

The present study is an attempt to reconcile the varying observations of earlier investigators on copper dissolution and a reinvestigation of the mechanism of extraction. The dissolution of copper was studied separately from the dissolution of copper by the copper ammine complex. The former was carried out in air-saturated and oxygen-saturated solutions of aqueous ammonia where the concentration of copper in solution was initially zero. The latter was carried out with copper as cupric ammine complex initially present in the solution and oxygen driven out of the system. The combined effect of oxygen and cupric ammine complex was also investigated. In addition to oxygen and copper concentration in solution, other parameters investigated were ammonia concentration, ammonium
carbonate concentration, and stirring velocity. The method used in this study was the rotating disc method. The rotating disc was advantageous because for laminar conditions the flow pattern and concentration distribution of the reactant in solution could be analyzed theoretically. It had the added advantage of a "uniformly accessible surface", a consequence of which was a uniformly dissolving surface. The experimental setup was designed to approximate the conditions of the theory and the experimental results were interpreted according to what might be expected from theoretical considerations.
REVIEW OF LITERATURE

The dissolution of metallic copper in aqueous ammonia has been the subject of a number of investigations over the past 50 years. Among those who have studied the kinetics of this reaction are Yamasaki (36), Lane and McDonald (19), Halpern (16), and Fisher and Halpern (12). To some extent this reaction was also studied by Dana (9), Vora (32), and Wu (35). Descriptions of the reactions involved in the dissolution process used by the Calumet and Tecla Mining Co., in Lake Linden, Michigan (3, 4), the Kennecott Copper Corporation (11), and the Universal Mineral and Metals, Inc., in Kansas City (37) are also available.

Yamasaki (36) rotated two copper plates at an equal distance from the axis of a platinum holder in a solution of aqueous ammonia. The plates were rotated vertically so that the plates rotated at nearly equal velocity. The air bubbled through the reaction vessel was first passed through a solution of caustic soda and three bottles of aqueous ammonia, in series, of the same initial concentration as the ammonia in the reaction vessel. The caustic soda was used to remove carbon dioxide from the air and the ammonia was used to compensate for the loss of free ammonia in the reaction vessel. Rotation was provided by an electric motor and speeds were generally at 1120 rpm. Ammonia concentrations were from 0.1 to 4 N.
Ammonium salts were also used in some runs. Solution temperature was mostly at 24.8°C. The rate of dissolution was measured by weighing the plates with an assay balance to determine the loss of copper after rotating the plates for a measured length of time. Prior to weighing, the plates were placed in water slightly acidified with sulfuric acid; washed with distilled water, alcohol, and ether; and then dried in a desiccator. In the region where the concentration of free cupric and hydroxyl ions did not disturb the system, Yamasaki observed that the dissolution of copper in aqueous ammonia involved two independent chemical reactions: (a) the oxidation of copper by oxygen, and (b) the oxidation of copper by the cupric ammine complex. It appeared to Yamasaki that the rate of the former reaction was proportional to the square root of the concentration of oxygen in solution and that the latter reaction was proportional to the concentration of cuprammonium compound, or

\[ Y = k_O \sqrt{C_{O_2}} + k_C C_{Cu} \]  

where \( Y \) was the dissolution rate, \( k_O \) and \( k_C \) were constants, \( C_{O_2} \) was the concentration of oxygen and \( C_{Cu} \) was the concentration of cupric ammine complex in solution. \( C_{Cu} \) was also equal to the concentration of copper in solution in the presence of oxygen since the cuprous complex was readily oxidized to the cupric form. Yamasaki proposed the following mechanism for copper dissolution in aqueous ammonia:
\[ \text{Cu} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} = \text{Cu}^{++} + 2\text{OH}^- \quad (2) \]

\[ \text{Cu}^{++} + a\text{NH}_3 = \text{Cu(NH}_3)_a^{++} \quad (3) \]

\[ \text{Cu(NH}_3)_a^{++} + b\text{NH}_3 + \text{Cu} = 2\text{Cu(NH}_3)_a^{+} \quad (4) \]

\[ 2\text{Cu(NH}_3)_{a+b}^{+} + (a-b)\text{NH}_3 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} = 2\text{Cu(NH}_3)_a^{++} + 2\text{OH}^- \quad (5) \]

The dissolution rate was the sum of the velocities of Equations 2 and 4 as expressed in Equation 1. The total velocity of the system was independent of the concentration of free ammonia and that of ammonium salts. The rate of the reaction was subject to a complex disturbance when the concentration of free cupric and hydroxyl ions increased which resulted from the accumulation of cuprammonium hydroxide in solution. When the concentration of cuprammonium hydroxide exceeded the saturation value, deposition of copper oxide and/or copper hydroxide occurred. Initially, the velocity of the reaction increased quite regularly until a maximum was reached after which the rate decreased. Smaller reaction rates were observed at reduced speeds. Yamasaki also suggested that the rate might be diffusion controlled but due to the dependence of dissolution rate on the square root of the oxygen concentration, which he observed, Yamasaki concluded otherwise.
Lane and McDonald (19) studied the effects of ammonia concentration, temperature, surface area, linear velocity, ionic strength, and viscosity on the dissolution rate of copper in aqueous ammonia. The cylindrical specimens were mounted on a stirrer such that all surfaces were at equal distance from the center and thus had equal surface velocities. Oxygen was passed through the reaction flask after passing through three gas washing bottles, one containing sodium hydroxide and two containing aqueous ammonia of the same molarity as that contained in the reaction flask. Ammonia concentrations used ranged from 0.23 to 0.689 mole/l. Solution temperature was mostly at 29.6°C. Samples were drawn from and returned to the reaction flask. The dissolved copper was determined by using a Lumetron photoelectric colorimeter. The increase in the rate of dissolution of copper at higher copper concentrations in solution as noted by Yamasaki (36) was not observed. Apparently, the oxidation of copper by the cupric ammine complex did not occur or was insignificant. The chemical reaction involved appeared to be first order with respect to ammonia. Results indicated that the dissolution process was composed of two parts. In the initial part of the reaction the dissolution of copper occurred at a rapid rate unhindered by the formation of insoluble corrosion products. In this region it appeared that the reaction was partially diffusion and chemically controlled. The latter part of the reaction was much slower
and was hampered by the presence of insoluble corrosion products on the surface of the specimen. There were several indications that the reaction was diffusion controlled. The reaction rate increased with the linear velocity of the rotating surface and the reaction rate decreased as the viscosity of the solution increased. In addition, the effect of temperature was small and less for smaller concentrations of ammonia. During the latter part of reaction where insoluble corrosion products appeared on the copper surface, Lane and McDonald argued that the diffusion of the reaction product from the surface of the metal to the bulk of the solution controlled the dissolution rate. A thermodynamic investigation was used to determine the rate controlling step in the initial part of the reaction. Possible combinations of oxidation-reduction cells were considered and the reaction that yielded the highest positive electrode potential with no characteristics that prevented the reaction from going to completion was regarded to be the most likely to occur. The following was considered to be the most likely rate controlling step:

$$\text{OH}^- + \text{OH}^- + \text{Cu} = \text{X}^-$$  \hspace{1cm} (6)

where $\text{X}^-$ is an activated complex which decomposes into $\text{CuO} + \text{H}_2\text{O}$. Reaction (Equation 6) is part of the oxidation of copper by oxygen which is the sum of the following equations:

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$$

$$4\text{OH}^- + 2\text{Cu} = 2\text{CuO} + 2\text{H}_2\text{O} + 4\text{e}^-$$.
Other than using oxygen, no other gas or gas mixture was used so that the effect of varying the concentration of oxygen on the dissolution rate of copper was undetermined.

Halpern (16) investigated the kinetics of the dissolution of copper in aqueous ammonia over a wide range of ammonia and oxygen concentrations and examined the effects of pH, temperature, stirring velocity, and the concentrations of \( \text{NH}_4^+ \) and other salts. The copper specimen was immersed in a solution of aqueous ammonia and a separate stirrer was provided. Oxygen pressure above the solution was controlled by a standard gas regulator. The pressure vessel was constructed entirely of stainless steel. Samples of solution were withdrawn during the course of the reaction through a sampling tube. Concentration of dissolved copper was determined with the use of a Beckman Model DU spectrophotometer. Solution temperature was 26°C. Halpern observed that: (a) at constant oxygen and ammonia concentrations, temperature, and stirring velocity, the amount of copper dissolved was proportional to the reaction time; (b) at low oxygen pressures the rate was determined by the transport of dissolved oxygen to the reaction surface and the rate was directly proportional to the pressure of oxygen above the solution, was independent of ammonia concentration and increased with stirring velocity; (c) at high oxygen pressures the reaction at the copper surface was controlling and the rate was dependent on the ammonia and ammonium ion concentrations and was not affected by changes in stirring velocity;
(d) the specific rate of dissolution (mg. Cu/(sq. cm.)(hr.)) was independent of solution volume and copper surface area;
(e) the reaction rate was independent of the copper concentration in solution. For the case where oxygen is present in the solution in excess so that the transport of oxygen to the surface of the copper is not the controlling mechanism, Halpern proposed the following mechanism for the dissolution process:

1. Adsorption of dissolved oxygen onto the copper surface:

\[ \text{Cu} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cu} + \text{O} \]

2. Reaction of an NH\(_3\) molecule or NH\(_4^+\) ion with the copper oxygen complex on the surface:

\[ \text{Cu} \ldots \text{O} + \text{NH}_3 \rightarrow \text{Cu} \left( \text{NH}_3 \right)^{++} + 2\text{OH}^- \]

or

\[ \text{Cu} \ldots \text{O} + \text{NH}_4^+ \rightarrow \text{Cu} \left( \text{NH}_3 \right)^{++} + 2\text{OH}^- \]

It was suggested that copper dissolves in the Cu(NH\(_3\))\(^{++}\) form, then reacts rapidly with other NH\(_3\) molecules to form higher ammines such as Cu(NH\(_3\))\(_4^{++}\) which are more stable.
In a subsequent study by Fisher and Halpern (12) the linearity of the plots of dissolution of pure copper versus time was confirmed. Halpern, Milants and Wiles (17) extended the investigation using other complex forming reagents and observations similar to those found using ammonia were obtained: (a) the specific dissolution rate was independent of the copper surface area and solution volume; (b) at low oxygen pressures the rate was proportional to oxygen pressure and independent of the concentration of the complexing agent; (c) at high oxygen pressures the rate was zero with respect to oxygen and first order with respect to the complexing agent.

Dana (9) investigated the extraction of pure copper filings in aqueous ammonia and a cation exchange resin at an elevated temperature. The resin used was Dowex 50W-X8. The temperature was 125°C; the resin to copper ratio was 1; and, the concentration of ammonia was 5N. In one case 500 ml. starting mixture was charged into a 1-l. stirred Parr pressure reactor and then sealed. In another, the mixture was charged into the Parr reactor with 50 psig oxygen. The amount of copper extracted after 2 hr. was about 5 times more with oxygen added to the system than without oxygen added.

Vora (32) and Wu (35) studied the dissolution of pure copper wire using a small glass column where air was bubbled through aqueous ammonia. The effects of copper concentration and the addition of ammonium salts were investigated. Like
Yamasaki (36), Vora and Wu found that the dissolution rate increased with increasing copper concentration in solution up to a maximum after which the rate decreased. Addition of ammonium salts increased the maximum concentration of copper corresponding to the point at which the dissolution rate started to drop. Furthermore, Wu reported that the maximum dissolution rate increased linearly with the concentration of ammonia and ammonium ions when both components were present in equal concentration.

The Calumet and Hecla Mining Co. had the first successful commercial application of an ammonia leaching process (3). A conglomerate ore containing native copper and no sulfides or oxidized copper minerals was crushed and free copper was removed by gravity concentration. The leaching solvent was a solution of copper ammonium carbonate. Benedict (3, 4) proposed the following mechanism:

1. Copper oxide or native copper in the presence of air dissolves in ammonium carbonate to form cupric ammonium carbonate according to

\[
\text{Cu} + \text{O} = \text{CuO}
\]

\[
\text{CuO} + (\text{NH}_4)_2\text{CO}_3 = \text{CuCO}_3 \cdot 2 \text{NH}_3 + \text{H}_2\text{O}.
\]

2. The cupric ammonium carbonate in the presence of native copper and without free access of air is reduced to the cuprous state:

\[
\text{CuCO}_3 \cdot 2\text{NH}_3 + \text{Cu} = \text{Cu}_2\text{CO}_3 \cdot 2\text{NH}_3.
\]
3. In the presence of air the cuprous ammonium carbonate rapidly oxidizes to the cupric state and is capable of dissolving more copper. The copper is then recovered by distillation whereby the ammonium carbonate is volatilized and recovered by absorption in water and the copper is precipitated as copper oxide which is sent to the smelter for refining:

$$\text{Cu}_2\text{CO}_3 \cdot 2\text{NH}_3 + \text{H}_2\text{O} + \text{Heat} = \text{CuO} + (\text{NH}_4)_2\text{CO}_3 .$$

The leaching process employed by the Kennecott Copper Corporation was very similar to that of Calumet and Hecla (11).

Universal Mineral and Metals, Inc. in Kansas City uses scrap copper as starting material. The copper is leached in a solution of ammonia, ammonium carbonate, and copper ammonium carbonate (37). The mechanism is considered to be:

$$\text{Cu} + (\text{NH}_4)_2\text{CO}_3 + 2 \text{NH}_3 + \frac{1}{2}\text{O}_2 = \text{Cu}(\text{NH}_3)_4\text{CO}_3 + \text{H}_2\text{O}$$

$$\text{Cu} + \text{Cu}(\text{NH}_3)_4\text{CO}_3 = \text{Cu}_2(\text{NH}_3)_4\text{CO}_3 .$$

The copper in solution is then reduced by hydrogen:

$$2 \text{Cu}(\text{NH}_3)_4\text{CO}_3 + \text{H}_2 = \text{Cu}_2(\text{NH}_3)_4\text{CO}_3 + \text{CO}_2 + 4\text{NH}_3 + \text{H}_2\text{O}$$

$$\text{Cu}_2(\text{NH}_3)_4\text{CO}_3 + \text{H}_2 = 2 \text{Cu} + \text{CO}_2 + 4\text{NH}_3 + \text{H}_2\text{O} .$$
THEORY OF THE ROTATING DISC SYSTEM

Fluid Flow

The development of the rotating disc system was presented by Levich (21) in a paper in 1942. To understand the theory, consider a system comprised of an infinite, horizontal plane coinciding with the plane $y = 0$ and rotating about the axis $r = 0$ with a constant angular velocity, $\omega$, in an infinite volume of fluid. Consider next the defining equations for the state of the fluid assuming that it is incompressible.

1. The continuity equation which expresses the law of conservation of matter:

$$ \nabla \cdot \vec{V} = \text{div} \vec{V} = \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} = 0 $$

where $\vec{V}$ is the fluid velocity vector.

2. The Navier-Stokes equation based upon a unit volume of fluid:

$$ \rho \frac{d\vec{V}}{dt} = -\nabla p + \mu \nabla^2 \vec{V} + \rho \vec{F} $$

where the left side of the equation is the product of the mass of the unit volume of fluid $\rho$ and its acceleration and the right side represents the sum of external forces acting on the unit and where $p$ is the pressure, $\mu$ the viscosity and $\vec{F}$ is any volume force such as gravity acting upon the element of fluid and where $\nabla^2$ is the Laplacian.
operator defined below.

\[ \nabla^2 = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \]

It is convenient to express the Navier-Stokes equation in terms of cylindrical coordinates since the rotating disc system possesses cylindrical symmetry. Refer to Fig. 1 for the coordinates and velocity components of the rotating disc system. Whitaker (34) gives the component forms of the Navier-Stokes equation in cylindrical coordinates:

**r-Direction**

\[
\rho \left( \frac{\partial V_r}{\partial t} + V_r \frac{\partial V_r}{\partial r} + \frac{V_\theta}{r} \frac{\partial V_r}{\partial \theta} - \frac{V_r}{r} + V_y \frac{\partial V_r}{\partial y} \right)
\]

\[= - \frac{\partial p}{\partial r} + \rho f_r + \mu \left[ \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} (r V_r) \right) + \frac{1}{r^2} \frac{\partial^2 V_r}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial V_\theta}{\partial \theta} \right]
\]

\[+ \frac{\partial^2 V_r}{\partial y^2} \]  

(7)
Lamina has an angular velocity, $\omega$, at $y = 0$.

Fig. 1. Coordinates and components of the rotating disc system.
Following the development by Riddiford (24) and Levich (20) the preceding equations can be simplified:

1. For nonturbulent, steady state conditions

\[ \frac{d\vec{v}}{dt} = 0. \]

2. By axial symmetry the flow is independent of \( \theta \) so that all derivatives with respect to this coordinate disappear.
3. In addition to being independent of $\theta$, $V_y$ is assumed to be independent of $r$.

4. Since the fluid is incompressible and the lamina is horizontal, $p$ is a function of $y$ only.

5. By considering angular velocities which generate forced convection of sufficient intensity, natural convection may be neglected so that $\overline{F} = 0$.

The component forms of the Navier-Stokes equation may then be written as

$$
\frac{\partial V_r}{\partial r} + \frac{V_r}{r} \frac{\partial V_r}{\partial y} - \frac{V_y^2}{r} = \nu \left[ \frac{\partial^2 V_r}{\partial r^2} + \frac{\partial}{\partial r} \left( \frac{V_r}{r} \right) + \frac{\partial^2 V_r}{\partial y^2} \right] \quad (10)
$$

$$
\frac{\partial V_\theta}{\partial r} + \frac{V_r}{r} \frac{\partial V_\theta}{\partial y} + \frac{V_r V_\theta}{r} = \nu \left[ \frac{\partial^2 V_\theta}{\partial r^2} + \frac{\partial}{\partial r} \left( \frac{V_\theta}{r} \right) + \frac{\partial^2 V_\theta}{\partial y^2} \right] \quad (11)
$$

$$
\frac{\partial V_y}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial y} + \nu \frac{\partial^2 V_y}{\partial y^2} \quad (12)
$$

where $\nu$ is the kinematic viscosity, $\mu/\rho$. The continuity equation becomes

$$
\frac{\partial V_r}{\partial r} + \frac{V_r}{r} + \frac{\partial V_y}{\partial y} = 0 \quad (13)
$$

The following boundary conditions must be satisfied:

$$
V_r = 0 \quad V_\theta = \omega r \quad V_y = 0 \quad \text{at } y = 0 \quad (14)
$$

$$
V_r = 0 \quad V_\theta = 0 \quad V_y = -X \quad \text{as } y \to \infty \quad (15)
$$
The last set of boundary conditions are due to the fact that close to the lamina the fluid acquires radial and tangential motion resulting in horizontal outflow. This flow of fluid must be balanced by an axial inflow, of negative sign, which must be constant at sufficiently great distance from the lamina since as \( y \) approaches infinity, \( V_r \) and \( V_\theta \) must approach 0.

\[
V_r = r \omega F (\delta) \quad (16)
\]

\[
V_\theta = r \omega G (\delta) \quad (17)
\]

\[
V_y = (\omega \nu)^{1/2} H (\delta) \quad (18)
\]

\[
p = -\rho \nu \omega P (\delta) \quad (19)
\]

where the independent variable is the dimensionless quantity

\[
\delta = \left( \frac{e}{v} \right)^{1/2} y \quad (17)
\]

Substituting the equations in 16 into the Navier-Stokes and continuity equations, the following equations are obtained:

\[
F^2 - G^2 + F'H = F'' \quad (18)
\]

\[
2 FG + G'H = G'' \quad (19)
\]

\[
HH' + 2F' = P' \quad (20)
\]

\[
2 F + H' = 0 \quad (21)
\]

The boundary conditions become

\[
F = 0, \ G = 1, \ H = 0, \ \text{at} \ \delta = 0 \quad (22)
\]

\[
F \rightarrow 0, \ G \rightarrow 0, \ H \rightarrow -\beta \ \text{as} \ \delta \rightarrow \infty \quad (23)
\]
where $\beta$ is the constant $\frac{X}{(\nu \omega)^{1/2}}$ to be determined.

An exact solution of these equations as suggested by Von Karman was obtained by Cochran (5). The functions $F$, $G$, and $H$ may be made to satisfy Equations 18 to 23 by series expansions of the form

$$F = F_0 + F_1 e^{-\beta \delta} + F_2 e^{-2\beta \delta} + F_3 e^{-3\beta \delta} + ...$$  \hspace{1cm} (24)

for large values of $\delta$ and

$$F = f_0 + f_1 \delta + f_2 \delta^2 + f_3 \delta^3 + ...$$  \hspace{1cm} (25)

for small values of $\delta$.

The form of these expansions is suggested by the boundary conditions. For example, as $\delta$ approaches infinity Equation 18 may be written as

$$-\beta F' = F''$$

which suggests the form $F = A e^{-\beta \delta}$. Similarly, as $\delta$ approaches infinity, $G$ acquires the form

$$-\beta G' = G''$$

which suggests that $G = B e^{-\beta \delta}$. As $\delta$ approaches zero, Equation 18 may be written as

$$-1 = F''$$
which gives the form

\[ F = c_1 + c_2 \delta + c_3 \delta^2 . \]

When the series expansions of \( F, G, H, \) and \( P \) are substituted into Equations 18 - 21 and the coefficients are equated, the number of unknown coefficients is reduced and for large values of \( \delta \) become

\[ F = F_1 e^{-\beta \delta} - \frac{(F_1^2 + G_1^2)}{2\beta^2} e^{-2\beta \delta} + \frac{F_1(F_1^2 + G_1^2)}{4\beta^4} e^{-3\beta \delta} + ... \] (26)

\[ G = G_1 e^{-\beta \delta} - \frac{G_1(F_1^2 + G_1^2)}{12\beta^4} e^{-3\beta \delta} + ... \] (27)

\[ H = -\beta + \frac{2F_1}{\beta} e^{-\beta \delta} - \frac{(F_1^2 + G_1^2)}{2\beta^3} e^{-2\beta \delta} + \frac{F_1(F_1^2 + G_1^2)}{6\beta^5} e^{-3\beta \delta} + ... \] (28)

and for small values of \( \delta \) become

\[ F = f_1 \delta - 1/2 \delta^2 - \frac{g_1}{3} \delta^3 - ... \] (29)

\[ G = 1 + g_1 \delta + \frac{f_1}{3} \delta^3 + ... \] (30)

\[ H = -f_1 \delta^2 + \frac{\delta^3}{3} + \frac{g_1}{6} \delta^4 + ... \] (31)

so that the only unknown coefficients are \( F_1, G_1, \beta, f_1 \) and \( g_1 \). The object then at this stage is to find \( F_1, G_1, \beta, f_1 \) and \( g_1 \) so that the functions \( F, G, H \) and the derivatives \( F' \) and \( G' \)
remain continuous when the two series are matched. Cochran solved the system of equations by numerical integration. He obtained

\[
\begin{align*}
F_1 &= 0.934 & G_1 &= 1.208 \\
\beta &= 0.886 & f_1 &= 0.510 & g_1 &= -0.616
\end{align*}
\]

The distribution of pressure \( P \) can be obtained from Equation 20

\[
\frac{\text{d}H}{\text{d}\delta} + \frac{2\text{d}F}{\text{d}\delta} = \frac{\text{d}P}{\text{d}\delta} . \tag{20}
\]

If \( P_o \) is the pressure at the surface of the lamina and Equation 20 is integrated using the boundary conditions

\[
H = 0, \quad F = 0
\]

at the surface, the following expression for \( P \) is obtained:

\[
P - P_o = \frac{1}{2}H^2 + 2F .
\]

Fig. 2 shows the functions \( F, G, \) and \( H \) graphically.

Convective Diffusion Equation

Solute dissolved in a moving fluid may be transported through it by two mechanisms. First, transport may be by molecular diffusion as a result of differences in concentration. Second, solute particles may be transported by entrainment in the moving fluid. Convective diffusion is a combination of these two transport mechanisms. If an imaginary unit plane is considered in the fluid, the flow of the matter due to molecular
Fig. 2. Plot of the functions $F$, $G$, and $H$ from Cochran's (5) solution.
diffusion is

\[ j_d = -D \nabla c \]

where \( D \) is the diffusion coefficient and \( c \) the number of particles per unit volume of liquid.

The flux of matter due to entrainment by the flowing stream is

\[ j_{\text{conv}} = c \bar{V} \]

where \( \bar{V} \) is the velocity of the fluid.

The total mass flux is then

\[ j = c \bar{V} - D \nabla c \ . \]

Next, consider an arbitrary volume \( V_o \) in the fluid. The number of particles passing through the surface \( S \) in one second is given by

\[ Q = - \int_S j \cdot \vec{n} \, dS \]

where the integral is taken over the surface \( S \) that surrounds the volume \( V_o \) and \( \vec{n} \) is the positive (outward drawn) normal to \( S \).

The change in the number of particles per unit volume per second is \( \frac{\partial c}{\partial t} \) so that

\[
\left[ \frac{\partial c}{\partial t} \right] \, dV_o = - \int_S j \cdot \vec{n} \, dS \ .
\]
But
\[ \int_s j \cdot \bar{n} \, dS = \int_v \nabla \cdot j \, dv \]

by the divergence theorem of Gauss, so that
\[ \int_0^t \frac{\partial c}{\partial t} \, dv = - \int_v \nabla \cdot j \, dv \]

and
\[ \frac{\partial c}{\partial t} = -\nabla \cdot j = \nabla \cdot (D \nabla c) - \nabla \cdot \overline{c} \overline{V} \]

\[ \nabla \cdot (D \nabla c) = D \nabla^2 c \]

\[ \nabla \cdot \overline{c} \overline{V} = (\nabla c) \cdot \overline{V} + c(\nabla \cdot \overline{V}) \]

But
\[ \nabla \cdot \overline{V} = 0 \]

if the fluid is incompressible, so that
\[ \frac{\partial c}{\partial t} + (\nabla c) \cdot \overline{V} = D \nabla^2 c \] \hspace{1cm} (32)

is the convective diffusion equation. The solution to this equation is greatly simplified if \( c \) is the independent of time. In this case the convective diffusion equation becomes

\[ (\nabla c) \cdot \overline{V} = D \nabla^2 c \] \hspace{1cm} (33)

Levich (20) gives the form of Equation 33 in cylindrical coordinates:
The solution to Equation 34 depends on the boundary conditions of the rotating disc system. Suppose the following boundary conditions prevail (the significance of these conditions as to the present investigation will be discussed later).

\[ c = c_0 \text{ at } y \to \infty \] (35)

where \( c_0 \) is the concentration in the bulk of the solution.

\[ c = 0 \text{ at } y = 0 \] (36)

At this point Levich (20) assumes that \( c \) is not a function of \( r \). Also, as in the fluid velocity vector, \( c \) is independent of \( \theta \) due to symmetry so that Equation 34 reduces to

\[ V_y \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} \]

or

\[ V_y \frac{dc}{dy} = D \frac{d^2 c}{dy^2} \] (37)

Let

\[ g = \frac{dc}{dy} ; \quad \frac{dg}{dy} = \frac{d^2 c}{dy^2} \quad V_y g = D \frac{dg}{dy} \]
Integrating,
\[ g = a_1 \exp \left( \frac{1}{D} \int_{0}^{Y} V_y \, dy \right) = \frac{dc}{dy} \]  \quad (38)

Integrating again,
\[ c = a_1 \int_{0}^{Y} \exp \left( \frac{1}{D} \int_{0}^{t} V_y \, dz \right) \, dt + a_2 \]  \quad (39)

From boundary condition 36 and Equation 39
\[ a_2 = 0 \]

And by boundary condition 35 and Equation 39
\[ c_0 = a_1 \int_{0}^{\infty} \exp \left( \frac{1}{D} \int_{0}^{t} V_y \, dz \right) \, dt \]  \quad (40)

It is convenient at this point to divide the interval of integration into two regions: from 0 to \( \varepsilon_0 \) and from \( \varepsilon_0 \) to infinity where \( \varepsilon_0 \) is the thickness of the hydrodynamic boundary layer on the disc surface. Within the boundary layer radial and tangential velocity components are present while beyond that layer only axial motion exists. Referring to Fig. 2 \( \varepsilon_0 \) may be taken as
\[ \varepsilon_0 = 3.6 \sqrt{\frac{V}{\omega}} \]  \quad (41)

since at values of \( \delta = 3.6 \), \( V_y \) attains more than 80 percent of its limiting value and \( V_\theta \) decreases to about 0.05 times its
value at the surface of the disc. The advantage of dividing the interval of integration will be apparent shortly.

\[ I = \int_0^\infty \exp \left( \frac{1}{D} \int_0^t V_y \, dz \right) \, dt = \int_0^{E_0} \exp \left( \frac{1}{D} \int_0^t V_y \, dz \right) \, dt \]

\[ + \int_{E_0}^\infty \exp \left( \frac{1}{D} \int_0^t V_y \, dz \right) \, dt = I_1 + I_2 . \]

For \( I_1 \), \( V_y \) is obtained from Equations 16 and 31:

\[ V_y = (\omega v)^{1/2} = (\omega v)^{1/2} \left( -f_1 \delta^2 + 1/3 \delta^3 + \frac{g_1}{6} \delta^4 + ... \right) \]

Neglecting higher order terms,

\[ V_y = (\omega v)^{1/2} (-0.510(\frac{\omega}{v})y^2) = \frac{-0.510\omega^{3/2}y^2}{v^{1/2}} . \]

Therefore,

\[ I_1 = \int_0^{E_0} \exp \left( \frac{1}{D} \int_0^t \left[ -0.510\omega^{3/2}y^2 \right] \frac{1}{v^{1/2}} \right) \, dy \, dt \]

\[ I_1 = \int_0^{E_0} \exp \left[ -\frac{\omega^{3/2}t^3}{5.88Dv^{1/2}} \right] \, dt . \] (42)

Substituting the following into Equation 42,
\[ u = \frac{\omega^{1/2} t}{\sqrt[3]{5.88 D^{1/3} \nu^{1/6}}} \]

\[ I_1 = \frac{1.81 D^{1/3} \nu^{1/6}}{\omega^{1/2}} \int_{0}^{\epsilon_o \omega^{1/2}} \frac{\epsilon \omega^{1/2}}{1.81 D^{1/3} \nu^{1/6}} e^{-u^3} du \]

\[ = \frac{1.81 D^{1/3} \nu^{1/6}}{\omega^{1/2}} \int_{0}^{2 \left(\frac{\nu}{D}\right)^{1/3}} e^{-u^3} du \]

since \( \epsilon_o = 3.6 \sqrt{\nu/\omega} \).

In liquids \( \nu \gg D \), so that \( \frac{\nu}{D} \gg 1 \), and since the integrand decreases rapidly for values of \( u \) greater than unity, the upper limit of integration may be replaced by infinity. Thus,

\[ I_1 = \frac{1.81 D^{1/3} \nu^{1/6}}{\omega^{1/2}} \int_{0}^{\infty} e^{-u^3} du . \]

The terms inside the integration sign may be expressed in terms of the gamma function by substituting \( t \) for \( u^3 \).
\[ \int_0^\infty e^{-u^3} du = \frac{1}{3} \int_0^\infty e^{-t^{2/3}} dt = \frac{1}{3} \Gamma \left( \frac{1}{3} \right) = \Gamma \left( \frac{4}{3} \right) = 0.89 . \]

Finally, 

\[ I_1 = \frac{1.612 D^{1/3} \nu^{1/6}}{\omega^{1/2}} . \]

Similarly, \( I_2 \) may be evaluated:

\[ I_2 = \int_\varepsilon_0^\infty \exp \left\{ \frac{1}{D} \int_0^t V_y dz \right\} dt . \]

In this interval, \( V_y \) is obtained from Equations 16 and 28:

\[ V_y = (\omega \nu)^{1/2} \left[ -\beta + \frac{2F_1 e^{-B}}{B} - \frac{(F_1^2 + G_1^2) e^{-2B}}{2B^3} + \ldots \right] \]

\[ V_y = (\omega \nu)^{1/2} (-\beta) \quad \text{as} \ \delta \to \infty \]

\[ V_y = -0.886 (\omega \nu)^{1/2} \]

so that

\[ I_2 = \int_\varepsilon_0^\infty \exp \left\{ \frac{1}{D} \int_0^t [-0.886 (\omega \nu)^{1/2}] \ dz \right\} dt \]

\[ = \int_\varepsilon_0^\infty \exp \left\{ -0.886 (\omega \nu)^{1/2} \frac{t}{D} \right\} dt \]
\[
I_2 = \frac{D}{0.886 (\omega v)^{1/2}} \exp \left( \frac{-3.2v}{D} \right) .
\]

Since \( v \gg D \), \( I_2 \) is negligible compared to \( I_1 \). Therefore,
\[
I = I_1 = \frac{1.612 D^{1/3} v^{1/6}}{\omega^{1/2}} .
\]

Recall that the solute concentration, \( c \), is expressed as
\[
c = a_1 \int_0^Y \exp \left( \frac{1}{D} \int_0^t V_y \, dz \right) \, dt
\]
and
\[
a_1 = \frac{c_0}{I}
\]
thus,
\[
c = \frac{c_0}{I} \int_0^Y \exp \left( \frac{1}{D} \int_0^t V_y \, dz \right) \, dt .
\]

The mass flux to the disc surface is
\[
j = D \left( \frac{\partial c}{\partial Y} \right)_{Y=0}
\]
\[
j = \frac{D c_0}{I} \exp \left( \frac{1}{D} \int_0^{t=y=0} V_y \, dz \right) = \frac{D c_0}{I}
\]
\[ j = \frac{D c \omega^{1/2}}{1.612 D^{1/3} \omega^{1/6}} = 0.62 D^{2/3} \omega^{-1/6} c_0 \]  

Equation 43 is the solution to the convective diffusion equation corresponding to a set of boundary conditions indicating a diffusion controlled reaction. The dependence of the flux to the square root of the angular velocity suggest a plot of flux versus \( \omega^{1/2} \). A diffusion controlled reaction will thus be indicated by a linear relationship on such a plot.

Solution to the Convective Diffusion Equation: Boundary Condition II

Consider the case when the following boundary condition is present at the surface of the disc:

\[ D \left( \frac{\partial c}{\partial y} \right)_{y=0} = k c_s^m ; \ c = c_s \ \text{at} \ y = 0 \]  

where \( c_s \) is the concentration at the disc surface, to be determined; \( m \) is the order of the reaction; and \( k \) the rate constant. Recalling Equation 39,

\[ c = a_1 \int_0^t \exp \left( \frac{V_y}{D} \right) \left. \frac{\partial V_y}{\partial y} \right|_0 \, dz \, dt + a_2 \]  

\( a_2 = c_s \) from boundary condition 44. Also,

\[ \left( \frac{\partial c}{\partial y} \right)_{y=0} = a_1 \]

therefore,

\[ D a_1 = k a_2^m . \]  

(45)
The boundary condition
\[ c = c_o \quad \text{as} \quad y \to \infty \]
still holds so that from Equation 39,
\[ c_o = a_1 \int_0^\infty \exp \left( \frac{1}{D} \int_0^t V_y \, dz \right) \, dt + a_2 \]
\[ c_o = a_1 I + a_2 \]
where
\[ I = \frac{1.612 \, D^{1/3} \, \omega^{1/6}}{\omega^{1/2}} \]
thus
\[ a_1 = \frac{c_o - a_2}{I} = \frac{c_o - c_s}{I} \]
and the mass flux to the disc surface becomes
\[ j = D \left( \frac{c_o - c_s}{I} \right) = k c_s^m \quad (46) \]

To determine the reaction order \( m \) and the reaction rate constant \( k \), the mass flux \( j \) is measured at two different angular speeds \( \omega \). By Equation 46
\[ c_s = c_o - \frac{j I}{D} \]
\[ j = k \left( c_o - \frac{j I}{D} \right)^m \quad (47) \]
With two values of $\omega$,

$$j_1 = k \left[ c_o - \frac{j_1 I_1}{D} \right]^m, \quad j_2 = k \left[ c_o - \frac{j_2 I_2}{D} \right]^m$$

$$m = \frac{\ln \left( \frac{j_1}{j_2} \right)}{\ln \left( \frac{c_o - \frac{j_1 I_1}{D}}{c_o - \frac{j_2 I_2}{D}} \right)} \quad (48)$$

and from Equation 47

$$k = \frac{j}{\left( c_o - \frac{j I}{D} \right)^m} \quad (49)$$

Equation 43 shows that a plot of $j$ versus $\omega^{1/2}$ is linear for a diffusion controlled reaction. A comparative plot of mass flux versus the square root of angular velocity for a reaction corresponding to boundary conditions 44 can be made by first determining the value of $c_s$. To determine $c_s$, Levich (20) adopts a method used by Frank-Kamenetskii (13). From Equation 46,

$$c_s^m - \frac{Dc_o}{kI} + \frac{Dc_s}{kI} = 0 \quad (50)$$
If the following substitutions are made:

\[ t = \frac{c_s}{c_o} \]  
(51)

\[ h = \frac{kT}{Dc_o^{1-m}} \]  
(52)

Equation 50 is reduced to

\[ t^m = \frac{1}{h} - \frac{t}{h} . \]  
(53)

For a value of \( h \), Equation 53 is the equation of a straight line with slope equal to \( -\frac{1}{h} \) and intercept on the \( t^m \) axis equal to \( \frac{1}{h} \). This is illustrated in Fig. 3 as the straight lines originating from \( t = 1 \). The curves on Fig. 3 represent \( t^m \) for various values of \( m \) and \( t \). These curves are plots of \( t^m \) versus \( t \) as differentiated from the straight lines which are plots of Equation 53. The points of intersections of the curves and the straight lines are solutions to Equation 53. Thus, for a value of \( m \) the points of intersection correspond to different values of \( h \). Knowing \( m \) and \( h \) from Equations 48, 49 and 52 the value of \( t \) is obtained from Fig. 3 and the value of the surface concentration \( c_s \) from Equation 51. As an example, if \( m \) is equal to 1

\[ t = \frac{1}{1 + h} \]
Fig. 3. Graphical solution of Equation 53
\[ c_s = \frac{c_0 D}{D + 1k} \]

\[ j = \frac{D(c_0 - c_s)}{1} = k c_s \]

\[ j = \frac{k c_0}{1 + 1kc_0} = \frac{Dc_0}{\left[ 1.61 \frac{D}{\sqrt{v}} \frac{1}{k} \right]} \]

so that

\[ j = \frac{b_1 \omega^{1/2}}{b_2 + b_3 \omega^{1/2}} \]

where \( b_1, b_2 \) and \( b_3 \) are constants. Fig. 4 is an illustration of Equation 55 where the constants are all made equal to 1 for convenience. Equation 54 may also be written as

\[ j = \left[ \frac{j_k}{1 + \frac{j_k}{j_D}} \right] \]

where \( j_k \) is equal to \( kc_0 \) and is the limiting value of the reaction rate which is the case when \( c_s \) is equal to \( c_0 \) and \( j_D \) is the limiting diffusional flux which is the case when \( c_s \) is equal to zero. Fig. 4 illustrates the transition between these two extremes. At low angular velocities, the reaction is diffusion controlled and as the velocity increases there is a smooth transition into the reaction controlled region.
Fig. 4. Transition from a diffusion controlled reaction to a chemical reaction controlled reaction. Plot of Equation 55 with all the constants equated to 1.
According to Levich (20) the transition from the diffusion controlled region to the reaction controlled region becomes more abrupt as the exponent m which is assumed to be 1 in Fig. 4 decreases.
EXPERIMENTAL INVESTIGATION

Apparatus

The rotating disc system was designed to approximate the requirements imposed by the conditions of the theory. The theory specifies a lamina of infinitesimal thickness and of infinite diameter, rotating with constant angular velocity in a fluid of infinite volume. Azim and Riddiford (1) reported that the first two conditions (i.e., a lamina of infinitesimal thickness and of infinite diameter) could be satisfied if the overall diameter of the disc was very much greater than the thickness of the hydrodynamic boundary layer and if the diameter of the working region was very much greater than the thickness of the diffusion boundary layer. Recalling Equation 41, the hydrodynamic layer is approximately

\[ \varepsilon_0 = 3.6 (\omega/v)^{1/2}. \]

For water at room temperature and with \( \omega = 100 \text{ rad./sec.} \),

\[ \varepsilon_0 \approx 3.6 \left( \frac{0.1}{10} \right) = 0.04 \text{ cm.} \]

With 2 and 3-in. diameter copper discs, 0.04 cm. is very small.

The thickness of the diffusion boundary layer may be obtained from the conditions in Equation 43.

\[ \varepsilon = \frac{Dc\omega}{J} = 1.61 \left( \frac{D}{v} \right)^{1/3} \left( \frac{\nu}{D} \right)^{1/2} \approx 0.5 \left( \frac{D}{v} \right)^{1/3} \varepsilon_0 . \]
For aqueous solutions at room temperature, $\varepsilon$ is of the order $10^{-3} \text{ cm.}$ (1). This value is very small compared to the diameter of the copper disc.

To approximate the condition of an infinite volume of fluid, the work of Gregory and Riddiford (14) on zinc-iodine systems was reviewed. Working with a disc 5.30 cm. in diameter and a vessel 12.5 cm. in diameter, their results were found to be independent of solution volume when the disc was situated at least 0.5 cm. from both the surface of the liquid and the bottom of the vessel. For the present investigation the inside diameter of the reactor was 16.4 cm. and the copper disc was submerged about 1 cm. from the surface of the solution which was 12 cm. deep.

The experimental setup is shown in Fig. 5. The glass reactor was 7 in. outside diameter and 6 in. high with 1/4 in. thick walls. An 8 in. by 8 in. Plexiglas flange, 1/4 in. thick, with a hole 6 in. in diameter was affixed by epoxy glue to the upper rim of the reactor. An 8 in. by 8 in. Plexiglas plate served as cover. The cover had an 11/32-in. diameter hole in the center for the shaft attached to the copper disc and a 3/4-in. diameter hole on one side for the oxygen probe, for temperature measurements with a mercury thermometer, and for obtaining samples. The sampling hole was plugged with a rubber stopper between readings and samplings. Between the Plexiglas cover and flange was a rubber gasket. When in use
Fig. 5. Experimental setup for rotating disc system
the cover and gasket were clamped to the square flange. A sidearm was made of 1-1/2 in. outside diameter glass tubing and was 18 in. high. A glass sparger was inserted on the sidearm and was connected with Tygon tubing to the ammonia saturators. The reactor and sidearm were connected by 5/8-in. diameter Tygon tubes near the bottom and near the level of the liquid surface when the reactor was filled with 2 l. of solution. The Tygon tubes were attached to nipples on one side of the reactor and on one side of the glass column. The distance from the side of the reactor to the side of the column was 5-1/2 in. The fluid was circulated through the sidearm by the bubbling action of the sparger. Fluid was admitted to the sidearm through the bottom tubing and left the sidearm through the upper tubing into the reactor. A rubber plug held the sparger in the sidearm and a piece of glass tubing served as a vent.

Different speeds of rotation at maintainable levels were provided by a GT 21 laboratory mixer connected to a GT 21 motor controller (Gerald K. Heller Company, Las Vegas, Nevada). The mixer was equipped with a slow shaft that could go up to 277 rpm and a fast shaft that could go up to 5000 rpm.

Two and 3-in. diameter copper discs were made from a copper sheet 0.04 in. thick. At the center of each of these discs was soft-soldered a cylindrical hub made of brass 5/16 in. in diameter and 5/8 in. long. The brass hub was threaded inside to a depth of about 3/8 in. to fit the threaded end of
a stainless steel shaft 8 in. long and 5/16 in. in diameter. The copper discs were polished with emery paper. The discs were made by the Instrument Shop of Iowa State University. It was necessary that only one face of the disc be exposed when in use. This was accomplished by coating the upper surface and brass hub with epoxy glue. The disc was viewed through a microscope to see if there were any flaws in the coating. If there were, the disc was recoated. The glue could be removed when desired, as when the disc were to be recoated, by soaking the disc in acetone or by immersing the disc in boiling water followed by soaking in acetone.

Caustic soda solution was used to remove carbon dioxide from the gas that was bubbled through the glass column connected to the reactor. To compensate for the loss of ammonia, the gas was first saturated by bubbling through two ammonia saturators. The caustic soda scrubber and the ammonia saturators were each fitted with a glass sparger. The rubber stoppers that were used as covers were held by masking tape to the bottles when the system was in operation. The rotameter, regulator, and manometer system provided means for control of the gas flow rate. The setup was calibrated with a wet test meter (Precision Scientific Co., Chicago, Illinois). By means of this system the concentrations of ammonia and oxygen in solution could be maintained.
Another equipment setup similar to the bubble reactor of Wu (35) and Vora (32) was used in a few runs. In these runs an attempt was made to duplicate run W69-NR-6 by Wu and to measure the oxygen concentration in solution during the course of the experiment. This system is shown in Fig. 6. The bubble reactor previously used by Wu and Vora was altered so as to accommodate a sidearm. This sidearm was used for the oxygen probe, for temperature measurements, and for obtaining samples. The valves and rotameter of Wu and Vora were used except for the valve going into the ammonia saturator which was rusty. The caustic soda scrubber and ammonia saturators of the rotating disc setup were also used. The air flow rate was recalibrated with a wet test meter and the equipment was then set to admit air at 1 l./min.

Materials

The following were the reagents and materials used in the research work described in this report:

**Acetone**

Obtained from bulk supply in Chemical Engineering Shop of Iowa State University. Manufacturer not known.

**Air**

Pressurized air was supplied through the main line in Sweeney Hall by the Physical Plant of Iowa State University, Ames, Iowa.
Fig. 6. Experimental setup for bubble reactor
Ammonia

Ammonium Hydroxide
Analytical Reagent 3256
Mallinckrodt Chemical Works

Ammonium Hydroxide
"Baker Analyzed" Reagent 9721
J.T. Baker Chemical Company
Phillipsburg, New Jersey

Ammonium carbonate

Purified Code 1280
General Chemical Division
Allied Chemical and Dye Corporation
New York, New York

Ammonium chloride

"Baker Analyzed" Reagent 0660
J.T. Baker Chemical Company
Phillipsburg, New Jersey

Ammonium sulfate

Analytical Reagent 3512
Mallinckrodt Chemical Works
St. Louis, Missouri

Copper

Sheet form from Instrument Shop, Iowa State University, Ames, Iowa. This copper source was analyzed by emission spectroscopy by Mr. Edward DeKalb of the Ames Laboratory. Among the impurities detected were traces of silver, iron and magnesium and faint traces of nickel and silicon. The total amount of these impurities was less than 0.1%.

Powder form
Purified Lot No. 37,556
J.T. Baker Chemical Company
Phillipsburg, New Jersey

Wire cable cord
Electrical grade 18 SWG
Consolidated Wire and Associate Company
Chicago, Illinois
Hydrochloric acid

Analytical Reagent 2612
Mallinckrodt Chemical Works
St. Louis, Missouri

Nitric acid

Analytical Reagent 2704
Mallinckrodt Chemical Works
St. Louis, Missouri

Nitrogen gas

Pre-purified nitrogen
Air Products and Chemical Inc.
Allentown, Pennsylvania

Oxygen gas

U.S.P. Oxygen
Cook's Welders Supply Inc.
Algona, Iowa

Sodium hydroxide

Analytical Reagent 7708
Mallinckrodt Chemical Works
St. Louis, Missouri

Water

Distilled water from the still installed in Room 324,
Sweeney Hall, Iowa State University, Ames, Iowa.

Analytical Methods

The copper in solution was analyzed with a Perkin Elmer
Model 290 atomic absorption spectrophotometer (18, 22, 23).
The standard solution was prepared using electrical grade
copper wire dissolved in ammonia. Copper samples were weighed
with a Mettler balance and dissolved in concentrated ammonium
hydroxide. These solutions were kept in stock and the standard
solution was prepared from them. The standard solution was 10 ppm in copper and 0.5 N in ammonia. The calibration curve was prepared by taking meter readings for solutions prepared as 0, 2.5, 5, 7.5, and 10 ppm copper and 0.5 N in ammonia from the stock solutions. Subsequent determinations of copper from unknown solutions were made by using 0.5 N aqueous ammonia as blank solution and 10 ppm copper in 0.5 N aqueous ammonia as standard.

The total ammonia in solution was determined by titration with standardized sulfuric acid (31).

Experimental Procedures

Dissolution with oxygen

The runs involving the dissolution of copper in aqueous ammonia with oxygen present in the solution were made with air and oxygen. The procedures involved were essentially the same. A 4-l. solution of aqueous ammonia of the desired concentration was made up for each run. Two l. were used as the initial reactor solution and 2 l. were used in the ammonia saturators. Initially, the shaft hole was covered with masking tape and the sampling hole was covered with a rubber stopper. Air or oxygen was then admitted into the reactor at 5.5 cu.ft./hr. The system was allowed to stabilize for 30 min. In the meantime, the oxygen analyzer (Beckman Fieldlab Oxygen Analyzer, Beckman Instruments, Fullerton, California) was stabilized and
calibrated (2). The calibration medium was distilled water which had been previously saturated with air through a glass sparger and allowed to stand overnight. The copper disc was also cleaned during this stabilizing period. The disc was prepared by rotating it in a solution of 3 N nitric acid for about 3 min. and then rinsing it thoroughly with distilled water. The desired angular velocity was obtained by rotating a similar disc outside the reactor. The motor controller was set for a suitable speed and to duplicate this setting the motor was unplugged from the controller without changing the setting and was plugged back in when the dissolution was started. After air had passed through the reactor for 30 min. the disc was placed inside the reactor but above the solution and as close to the reactor cover as possible and the system was further allowed to stabilize for another 30 min. The solution temperature and oxygen concentration were read just before the end of this period. The disc was then lowered to a position slightly above the solution and the motor was connected to the motor controller at the previous setting. While already spinning the disc was immersed in the reactor solution. Time zero was the instant the disc touched the liquid. Approximately 8-ml. samples were pipetted through the sampling hole every 10 min. A 25-ml. pipette was used for this purpose in order to obtain samples rapidly. The samples were placed in test tubes and covered with rubber stoppers until they were analyzed with
the atomic absorption spectrophotometer. For air, most runs were for 1 hr. but some runs were for 40 min. The latter were runs made at higher speeds where the concentration of copper was more than 10 ppm after 1 hr. Such a high concentration would require dilution of the samples to determine the copper content. For oxygen, 1 hr. and 30 min. runs were made. Some of the samples obtained in the runs where oxygen was used were diluted with 0.5 N aqueous ammonia before they were analyzed for their copper content. For example, 5 ml. was measured from the 8-ml. sample obtained during the run and diluted with 5 ml. of 0.5 N aqueous ammonia. Measurements in this case were made with a 5-ml. pipette.

After the last sample for a run was taken the disc was raised from the reactor solution, then the motor was stopped and the disc and shaft were detached from the motor. The disc was examined and rinsed thoroughly with distilled water then dried with Kimwipes. Observations on the appearance of the disc surface were recorded—whether the disc looked uniformly dissolved and clean or whether there were deposits or divisions. The disc was then covered with Kimwipes, detached from the shaft and stored until the next run. After this was done the air or oxygen supply was closed and the ammonia saturators and reactor emptied of their contents. The reactor was either rinsed with a solution of aqueous ammonia or washed with Vel detergent and water and then rinsed thoroughly with distilled water. The glass sparger used in the reactor sidearm was
rinsed with distilled water and soaked in a solution of aqueous ammonia until the next run.

**Dissolution with cupric ammine complex**

A set of experiments was also made to investigate the rate of dissolution of copper by the cupric ammine complex. In addition to copper concentration in solution the parameters investigated were ammonia and ammonium carbonate concentrations. The runs were conducted in essentially the same manner as the runs using oxygen with pre-purified nitrogen substituted for oxygen. Starting solutions high in copper content were prepared by dissolving purified copper powder in approximately 2 N aqueous ammonia. Air was bubbled through the solution by means of a glass sparger after passing through a solution of sodium hydroxide and an ammonia saturator. The solution was stirred with a magnetic stirrer. The copper-rich solution was filtered through a Büchner funnel fitted with two layers of filter paper. For a desired mixture, 2200 ml. was prepared with 2000 ml. serving as the initial reactor solution and 200 ml. used in the determination of the initial copper and ammonia concentrations. The system was stabilized for 1 hr. and the run itself lasted for another hour. The solution temperature and oxygen concentration were measured at the start, middle, and end of the run. Angular velocity was measured at 5 min. from the start and every 10 min. thereafter. The total ammonia in the final and initial solutions were determined by titration with sulfuric
acid to the methyl orange endpoint. Near the endpoint the sample faded sharply from a blue-green color to clear yellow so that the cupric ammine complex was very likely broken by the acid. The initial and final solutions were diluted with approximately 0.5 N ammonia and analyzed for their copper content with the atomic absorption spectrophotometer. Solutions whose total ammonium carbonate concentrations exceeded 0.1 M were not checked for total ammonia.

**Dissolution of copper wire in a bubble reactor**

The bubble reactor experiment involved the dissolution of a measured length of copper wire in an air-saturated solution which was 0.5 N in ammonia and 0.1 M in ammonium carbonate. A trial run was first made where the system was allowed to run for 2 1/2 hr. with air flow rate at 1 l./min. The two ammonia saturators each filled with 1 l. of 0.5 N aqueous ammonia and the caustic soda scrubber of the rotating disc setup were used. Samples of the original and final solution were analyzed for ammonia by titrating with sulfuric acid to the methyl orange endpoint. When no noticeable change in total ammonia concentration was found, the actual runs were made. Electrical grade copper wire measuring 57 1/8 in. was used. The wire was folded to about a length of 6 in. and cleaned by soaking in approximately 0.5 N ammonia for 10 to 15 min. and then soaking in acetone until the start of the run. To start the run, the column was first filled with 220 ml. of starting solution. The
air flow rate was then adjusted to 1 l./min. Before putting the copper wire into the solution the oxygen concentration and temperature were measured through the sidearm. The folded wire was attached to a Nylon line and starting time corresponded to the moment the wire was immersed in the solution. Every 15 min. a 1-ml. sample was taken and the oxygen concentration and temperature were measured immediately after taking each sample. The run was for a total of 2 hr. The 1-ml. samples were placed directly in flasks partially filled with 0.5 N aqueous ammonia. Guided by the results of Wu (35) and the first trial run, the first 1-ml. sample was placed in a 100 ml. volumetric flask and the last sample was placed in a 2000-ml. volumetric flask. At the end of the run the flasks containing the samples were filled with 0.5 N aqueous ammonia and analyzed later for their copper content. Shut down procedure started by removing the copper wire from the bubble reactor. The wire was examined and rinsed with distilled water. The appearance of the wire was noted. The air supply was closed and the reactor and ammonia saturators were emptied of their contents. The bubble reactor was washed with Vel detergent and water then washed with distilled water. The reactor was filled with about 220 ml. solution of aqueous ammonia and attached back to the air supply. Air was admitted into the reactor for about 15 min. before it was finally emptied to be ready for the next run.
Testing and Development of the System

Prior to the construction of the reactor described previously an open beaker of similar dimensions was used for a reaction vessel with the copper disc. Fine resin particles and confetti were mixed with water to get a visual picture of the flow pattern when the disc was rotated in the solution. According to Levich (20) laminar conditions exists up to a Reynolds number of $10^4$ to $10^5$ (Reynolds number expressed as $\frac{kr^2\omega}{\nu}$ where $r$ is the radius of the disc, $\omega$ is the angular velocity and $\nu$ is the kinematic viscosity of the fluid) with a minimum of eccentricity. Different volumes of solutions were used. With a 2-in. diameter disc it was thought that the angular velocity should be below 150 rpm in order to stay in the laminar region. For aqueous solutions this angular velocity would correspond to a peripheral Reynolds number of about $10^4$. Since this value was a theoretical estimate, a more accurate means of determining the onset of turbulence was sought. Since the disc surface is uniformly accessible at laminar conditions, it should dissolve uniformly. The disc was rotated at different speeds in a solution of about 0.5 N aqueous ammonia. The disc was rotated for about 3 min. and the angular velocity was measured by taking the time it took for the disc to make 50 revolutions. For speeds above 150 rpm the disc was attached to the fast shaft of the motor and the angular velocity of the show shaft was measured so that with a
gear ratio of 18 to 1 the actual speed was 18 times that of the slow shaft. A chalk mark was made on the shaft as a guide for the actual counting of disc revolutions. Up to about 400 rpm, a 2-in. disc looked uniformly dissolved. At higher speeds the surface exhibited two regions. The approximately circular inner region was darker than the outer annular region which was nearly of the same metallic color as the disc before dissolution. This characteristic was evident in the 3-in. disc at lower speeds. In subsequent runs this phenomenon was also observed. Fig. 7 illustrates these results. The appearance of the division in the disc surface was interpreted to be the onset of turbulence. For a 2-in. disc, laminar conditions could be maintained up to about 400 rpm. The division on the disc surface was not observed up to this angular velocity. The peripheral Reynolds number corresponding to 400 rpm for a 2-in. disc is $1.64 \times 10^4$. The Reynolds number at the boundary between the two regions for the tracings in Fig. 7 are shown in the following table:

<table>
<thead>
<tr>
<th>Disc diam.</th>
<th>Run</th>
<th>Angular velocity</th>
<th>Reynolds no. at boundary $\times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>in.</td>
<td></td>
<td>rpm</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>110-1</td>
<td>726</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>113-1</td>
<td>671</td>
<td>2.8</td>
</tr>
<tr>
<td>3</td>
<td>122-9</td>
<td>246</td>
<td>1.8</td>
</tr>
<tr>
<td>3</td>
<td>122-10</td>
<td>406</td>
<td>4.8</td>
</tr>
</tbody>
</table>
Fig. 7. Tracings of copper surface after dissolution in 0.5 N aqueous ammonia beyond the laminar regime
The values of the Reynolds number in Table 1 were calculated by using an approximate average radius of the darker inner region on the disc surface. The variation of the critical Reynolds number obtained was probably caused by the imperfections of the system. At high speeds, as in run 122-10 which was with a 3-in. disc, a vortex formed around the shaft extending to the coated upper portion of the disc. The vortex formation could have affected the dissolution of the copper surface especially near the edges. A slight wobbling of the shaft was also noticeable. The vortex formation was less evident with the 2-in. disc and did not generally extend to the copper disc itself.

The trial runs with the rotating disc system were with air-saturated solutions of 0.5 N aqueous ammonia and a 2-in. diameter copper disc. These runs were made to determine whether the results could be reproduced and whether the ammonia and oxygen levels could be maintained. The reactor was filled with 2 l. of 0.5 N aqueous ammonia. The ammonia saturators were each filled with 1 l. of the same solution as in the reactor. Table 2 shows the data taken during the blank run. Samples measuring 10 ml. were pipetted every hour from the reactor and titrated with standardized sulfuric acid. This run indicated that the ammonia concentration in the reactor was maintainable for at least 4 hours at 0.5 N with the saturators. Should 100 ppm of copper dissolve in solution,
only 0.0063 mole of ammonia would be required to form the copper tetramine complex.

The following table shows the oxygen concentration in solution for runs made with the 2-in. copper disc rotating at about 60 rpm after a stabilization time of 1 hr.

Table 3. Oxygen concentration in air-saturated solution of 0.5 N aqueous ammonia

<table>
<thead>
<tr>
<th>Time, min.</th>
<th>Run 58</th>
<th>Run 59</th>
<th>Run 60</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7.95</td>
<td>8.00</td>
<td>8.05</td>
</tr>
<tr>
<td>20</td>
<td>7.95</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
<td>30</td>
<td>7.95</td>
<td>7.80</td>
<td>8.05</td>
</tr>
<tr>
<td>40</td>
<td>8.05</td>
<td>7.85</td>
<td>8.05</td>
</tr>
<tr>
<td>50</td>
<td>7.95</td>
<td>7.90</td>
<td>8.15</td>
</tr>
<tr>
<td>60</td>
<td>7.95</td>
<td>7.95</td>
<td>8.15</td>
</tr>
</tbody>
</table>
These oxygen concentrations were obtained by immersing the sensor of the oxygen analyzer into the solution without agitation other than that provided by the rotating disc and the bubbling action of the air passing through the sparger. Agitation of the sensor by hand to increase the relative velocity between liquid and sensor could give readings up to 8.4 ppm. The oxygen concentrations listed in Table 3 vary but the differences are less than 5 percent. This variation was thought to be sufficiently small to meet the requirement of a constant oxygen concentration in solution.

The first measurements of the rate of copper dissolution at about 60 rpm were inconsistent. It was suspected that the surface of the disc was not initially clean or that it was not at the same initial condition during each run. This occurred when a commercial household cleaner, Steel Bright, was used for cleaning the disc. To find a more suitable way of cleaning the disc, sulfuric acid, nitric acid, ammonium chloride, ammonium hydroxide in a nitrogen atmosphere, and ammonium hydroxide with a cation exchange resin were tried. Of these methods, 5 N sulfuric acid and 3 N nitric acid both produced reproducible results. The results of the runs where 5 N sulfuric acid was used to clean the disc are shown in Fig. 6. The epoxy coating of the disc, however, was more stable with the 3 N nitric acid so that this method of cleaning was adopted. The results in the subsequent runs discussed in the bulk of this report were obtained using 3 N nitric acid as the cleaning
Fig. 8. Trial runs for dissolution of 2-in. diameter copper disc in 2 l. of air-saturated solution of 0.5 N aqueous ammonia. Disc cleaned with 5 N H₂SO₄. Solution temperature = 24°C; oxygen in solution = 8 ppm
Measurement and Interpretation of Dissolution Rates

Dissolution with oxygen

Air-saturated solutions The first set of experiments were made to measure the dissolution rates of a 2-in. diameter disc in an air-saturated solution of 0.5 N aqueous ammonia at different angular velocities. Since the results of this study would be compared to the findings by earlier investigators 0.5 N was chosen to be the concentration of ammonia - a value used also by all the previously mentioned workers. Yamasaki (36) worked with ammonia concentrations ranging from 0.1 to 4 N; Lane and McDonald (19) from 0.23 to 0.689 N; Halpern (16) from 0.26 to 1.73 N; and, 0.5 N aqueous ammonia was one of the solutions both Vora (32) and Wu (35) worked with. The procedure followed in making a run is described in the section on procedures. The experimental setup is shown in Fig. 5. The conditions used during these runs are summarized in Fig. 9 and Table 4. Four liters of 0.5 N aqueous ammonia were prepared. Two liters were used as initial reactor solution and 2 l. used in the ammonia saturators. The runs were made with angular velocities of only up to 400 rpm in order to stay in the laminar regime. Fig. 9 shows the results of a series of runs at different angular velocities. The angular velocities
Fig. 9. Dissolution of 2-in. diameter copper disc in 2 l. of air-saturated solution of 0.5 N aqueous ammonia. Solution temperature = 24°C; oxygen in solution = 8 ppm.
Table 4. Summary of data for runs using air (oxygen in solution = 8 ppm, initial copper in solution = 0, solution temperature = 24°C)

<table>
<thead>
<tr>
<th>Run</th>
<th>Disc dia., in.</th>
<th>NH₃ normality</th>
<th>Length of run, min.</th>
<th>Cu conc. at end of run, ppm</th>
<th>(Angular velocity, rpm)⁴</th>
<th>Dissolution rate jₑ x 10⁷ g. Cu/(sq. cm.)(sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66-1</td>
<td>2</td>
<td>0.5</td>
<td>60</td>
<td>5.75</td>
<td>8.00</td>
<td>1.59</td>
</tr>
<tr>
<td>71</td>
<td>2</td>
<td>0.5</td>
<td>40</td>
<td>9.30</td>
<td>20.0</td>
<td>3.85</td>
</tr>
<tr>
<td>72</td>
<td>2</td>
<td>0.5</td>
<td>40</td>
<td>5.70</td>
<td>12.6</td>
<td>2.35</td>
</tr>
<tr>
<td>73</td>
<td>2</td>
<td>0.5</td>
<td>40</td>
<td>7.25</td>
<td>15.7</td>
<td>3.01</td>
</tr>
<tr>
<td>78</td>
<td>2</td>
<td>0.5</td>
<td>60</td>
<td>7.05</td>
<td>4.31</td>
<td>0.823</td>
</tr>
<tr>
<td>82</td>
<td>2</td>
<td>0.5</td>
<td>60</td>
<td>3.15</td>
<td>4.28</td>
<td>0.864</td>
</tr>
<tr>
<td>83</td>
<td>2</td>
<td>0.5</td>
<td>60</td>
<td>6.00</td>
<td>7.82</td>
<td>1.64</td>
</tr>
<tr>
<td>84</td>
<td>2</td>
<td>0.5</td>
<td>30</td>
<td>4.20</td>
<td>11.1</td>
<td>2.31</td>
</tr>
<tr>
<td>85</td>
<td>2</td>
<td>0.5</td>
<td>30</td>
<td>5.30</td>
<td>14.7</td>
<td>2.91</td>
</tr>
<tr>
<td>86</td>
<td>2</td>
<td>0.5</td>
<td>30</td>
<td>7.35</td>
<td>19.6</td>
<td>4.03</td>
</tr>
<tr>
<td>88</td>
<td>2</td>
<td>1.0</td>
<td>60</td>
<td>6.10</td>
<td>8.20</td>
<td>1.67</td>
</tr>
<tr>
<td>89</td>
<td>2</td>
<td>1.0</td>
<td>60</td>
<td>6.10</td>
<td>8.18</td>
<td>1.67</td>
</tr>
<tr>
<td>91</td>
<td>2</td>
<td>1.0</td>
<td>60</td>
<td>3.20</td>
<td>4.16</td>
<td>0.892</td>
</tr>
<tr>
<td>92</td>
<td>2</td>
<td>1.0</td>
<td>60</td>
<td>2.90</td>
<td>3.93</td>
<td>0.796</td>
</tr>
<tr>
<td>93-1</td>
<td>2</td>
<td>1.0</td>
<td>30</td>
<td>4.45</td>
<td>11.8</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

^aDisc no. 2.
indicated were the values obtained by taking the average of the measurements made between samplings. Maximum and minimum speeds were within ± 5 percent of the average value. Fig. 9 shows that the dissolution of copper was linear with time. The dissolution rate at a certain angular velocity was obtained by dividing the slope of the corresponding line in Fig. 9 by the surface area of the disc and multiplying by the volume of the solution. The surface area of a 2-in. disc is 20.25 sq. cm. Thus, the dissolution rate of copper at 64 rpm was:

\[
\text{Dissolution rate} = \left( \frac{5.8 \text{ mg.Cu/l.}}{60 \text{ min.}} \right) \left( 2 \text{ l.} \right) \left( \frac{1}{20.25 \text{ sq. cm.}} \right)
\]

\[
= 9.54 \times 10^{-3} \text{ mg. Cu/ (sq. cm.) (min.)}
\]

\[
= 1.59 \times 10^{-7} \text{ g. Cu/(sq. cm.) (sec.)}
\]

The dissolution rates corresponding to all these runs were obtained in this manner and are listed in Table 4. The change in volume of the reactor solution as a result of taking an 8-ml sample every 10 min. was negligible.

The dependence of the dissolution rate upon angular velocity suggested a diffusion-controlled reaction. Recalling Equation 43,

\[
j = 0.62 D^{2/3} \nu^{-1/6} \omega^{1/2} c_o
\]

the mass flux \( j \) refers to the rate at which the limiting reactant is transported to the surface of the disc. Since this is the slowest step for a diffusion controlled reaction, the
rate at which the product is formed is proportional to this value. The product in this case, is the cupric ammine complex and the rate at which it is formed is proportional to the mass flux of the limiting reactant. Consider the following mechanism for the dissolution of copper:

\[
\begin{align*}
\text{Cu} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} & = \text{Cu}^{++} + 2 \text{OH}^- \quad (56) \\
\text{Cu}^{++} + 4 \text{NH}_3 & = \text{Cu}(\text{NH}_3)_4^{++} \quad (57)
\end{align*}
\]

If oxygen were the reactant whose diffusion from the bulk of the liquid to the surface of the disc were limiting, then the mass flux \(j_o\) of oxygen to the surface of the disc is given by Equation 43. The rate at which the copper goes into solution as the copper ammine complex is proportional to the mass flux of oxygen, \(j_o\). If the dissolution rate of copper is called \(j_{\text{cu}}\), then \(j_{\text{cu}}\) is related to \(j_o\) by the stoichiometry of the system. Since \(j_o\) is proportional to the square root of angular velocity then \(j_{\text{cu}}\) is also proportional to the square root of angular velocity. Similarly, if ammonia were the reactant whose diffusion from the bulk of the solution to the surface of the disc were limiting, then the mass flux \(j_a\) of ammonia to the surface of the disc is given by Equation 43. In any case, the dissolution rate \(j_{\text{cu}}\) would still be proportional to \(\omega^{1/2}\). A series of copper dissolution rates, \(j_{\text{cu}}\), were obtained from Fig. 9. A plot of \(j_{\text{cu}}\) versus \((\text{rpm})^{1/2}\) is shown in Fig. 10.
Fig. 10. Variation of dissolution rate with square root of angular velocity for 0.5 N aqueous ammonia. Solution temperature = 24°C; oxygen in solution = 8 ppm; 2-in. diameter disc
Additional points on the graph were obtained from replicate runs where only the final solutions were analyzed for their copper content. The dissolution rates computed from these replicate runs were obtained by taking the slope of the line determined by the origin and the point corresponding to the final concentration of copper in solution and the corresponding time. These results as well as others obtained with air-saturated solutions which will be discussed later are summarized in Table 4. The linear dependence of dissolution rate upon the square root of angular velocity indicated that the transport of one of the reactants to the surface of the disc was indeed controlling. This reactant could be either oxygen or ammonia.

At this stage of the investigation one way to tell whether oxygen or ammonia was the limiting reactant was to apply Equation 43 for both reactants. When this was done, the values obtained could be compared to values found in the literature. The reactant whose diffusivity as calculated by using Equation 43 came closer to the literature value would then be likely the limiting reactant. The kinematic viscosity is a property of the solution and may be taken as 0.01 sq. cm./sec. which is the kinematic viscosity of water at 20°C (33). The dissolution rate $j_{cu}$ was measured for a given run and $j_o$ and $j_a$ were determined by the stoichiometry according to Equations 56 and 57. From Fig. 10 $j_{cu}$ is $4.00 \times 10^{-7}$ g. cu./(sq. cm.)(sec.) with $\omega^{1/2}$ at 20. The concentration $c_o$ was $8.0 \times 10^{-3}$ mg./cu. cm.
for oxygen and 0.5 N or 8.5 mg./cu. cm. for ammonia. The corresponding diffusivities are shown in the following table.

Table 5. Diffusivities of oxygen and ammonia

<table>
<thead>
<tr>
<th></th>
<th>D calc. x 10^5, sq. cm./sec.</th>
<th>D literature x 10^5, sq. cm./sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>5.57</td>
<td>1.98^a</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.0014</td>
<td>--</td>
</tr>
</tbody>
</table>

^aFrom Siver and Kabanov (27).

No value of ammonia diffusivity was found in the literature to compare to that which was calculated. However, the order of magnitude of diffusivity of molecules and ions in aqueous solutions is 10^-5 to 10^-6 sq. cm./sec. (20). Therefore, the calculated orders of magnitude of diffusivity indicate that the dissolution rate was controlled by the transport of oxygen from the bulk of the solution to the surface of the copper disc rather than by that of ammonia.

Referring again to Equation 43, j varies linearly with \( c_0 \) at constant angular velocity. Another way of determining whether oxygen or ammonia was the limiting reactant would then be to repeat the experiments with the 2-in. disc in air-saturated solutions but with a different ammonia concentration.
According to Equation 43, doubling the concentration of the reactant whose transport from the bulk of the solution to the surface of the disc is controlling would double the dissolution rate. The second set of experiments was almost the same as the first except for the ammonia concentration which was raised from 0.5 to 1.0 N. The ammonia concentration was maintainable at 1 N in the reactor for at least 4 hr. by filling the first ammonia saturator with 1 l. of 1.5 N aqueous ammonia and the second saturator with 1 l. of 1 N solution. As with the experiments using 0.5 N ammonia, 1-hr. and 30-min. runs were made with samples taken every 10 min. and measurements of angular velocity made between samplings. In the first run, the oxygen concentration was also checked between samplings. Replicates were made where only the final solutions were analyzed for their copper content. Fig. 11 shows the results of spinning a 2-in. diameter disc at various speeds. Dissolution rates were calculated and compared with the results obtained with the 0.5 N ammonia solutions. Fig. 12 is a combined plot of dissolution rate versus square root of angular velocity for both concentrations of ammonia. A statistical analysis made to compare the slope of the line determined by the data points for the 1.0 N solutions and the slope of the line determined by the data points for the 0.5 N solutions as plotted in Fig. 12 showed that the difference of the slopes was not significant at the 0.05 level. This eliminated the
Fig. 11. Dissolution of 2-in. diameter copper disc in 2 l. of air-saturated solution of 1.0 N aqueous ammonia. Solution temperature = 24°C; oxygen in solution = 8 ppm
Fig. 12. Variation of dissolution rate with square root of angular velocity for 1.0 and 0.5 N aqueous ammonia. Solution temperature = 24°C; oxygen in solution = 8 ppm; 2-in. diameter disc
possibility that the reaction was controlled by the transport of ammonia from the bulk of the solution to the surface of the disc. The results obtained when the concentration of oxygen was changed from 8 ppm to 40 ppm will be discussed in the subsection on oxygen-saturated solutions.

A series of runs was also made in air-saturated solutions of aqueous ammonia using a 3-in. diameter disc. Ideally, the specific dissolution rate of copper should not vary with total surface area. This set of experiments was then made to determine how closely the experimental setup approached ideality. The procedure and conditions for this set of runs were the same as those for the 0.5 N aqueous ammonia except that the 3-in. disc was substituted for the 2-in. disc. Stabilization time was for 1 hr. One-hr. and 30-min. runs were made with samples taken every 10 min. Fig. 13 is a plot of the results of these runs at various angular velocities. The dissolution rates were determined from this graph and Fig. 14 is a plot of dissolution rate versus square root of angular velocity. A combined plot for both 2-in. and 3-in. discs is shown in Fig. 15. This set of experiments show that the specific rate of copper dissolution is slightly higher for a 3 in. disc than for a 2-in. disc. A statistical analysis made of this plot showed that the difference in the slope determined by the data points for the 3-in. disc and the slope determined by the data for the 2-in. disc was significant at the 0.05 level. In the
Fig. 13. Dissolution of 3-in. diameter copper disc in 2 l. of air-saturated solution of 0.5 N aqueous ammonia. Solution temperature = 24°C; oxygen in solution = 8 ppm
Fig. 14. Variation of dissolution rate with square root of angular velocity for 0.5 N aqueous ammonia using a 3-in. diameter disc. Solution temperature = 24°C; oxygen in solution = 8 ppm
Fig. 15. Variation of dissolution rate with square root of angular velocity for 0.5 N aqueous ammonia using a 2-in. and a 3-in. disc.
statistical analysis, only the first four data points for the 3-in. disc were used in order for the comparison to be made within the laminar regime. The difference in the specific dissolution rates for the 3-in. and 2-in. discs might be attributed to the imperfections of the system. A slight wobbling of the disc was noticeable when the disc was in motion and in the 3-in. disc this was aggravated by the disc's larger diameter. This wobbling could have resulted in additional agitation that was more pronounced in the 3-in. disc than in the 2-in. disc at the same angular velocity. The discrepancy may also be attributed to edge effects. Ideally, the disc should be infinite in size and in an infinite volume of solution so that the reactants could approach the disc only from a normal direction. In reality, the discs' dimensions were finite so that an additional influx of reactants could have come from the edges of the discs. This edge effect was probably greater on the 3-in. disc than the 2-in. disc. The bulk of this study, however, was with a 2-in. disc. The slight difference in dissolution rates due to a change in disc diameter was therefore not to be accounted for. The errors due to the imperfections of the system were assumed to cancel out since only a 2-in. disc was used for the remainder of the investigation.

Oxygen-saturated solutions In the experiments using air, it was observed that the dissolution rate was diffusion
controlled and that the limiting reactant was oxygen. There were two indications that oxygen was the controlling factor and not ammonia: (a) the plausibility of the diffusivity value obtained for oxygen and the corresponding improbability of the diffusivity obtained for ammonia if it were in fact the limiting reactant; (b) the independence of dissolution rate with ammonia concentration. A third means of showing that the reaction was indeed limited by the diffusion of oxygen from the bulk of the solution to the surface of the copper disc would be to increase the concentration of oxygen in solution; and, if oxygen were indeed the limiting reactant the dissolution rate of copper should correspondingly increase. The next set of experiments, therefore, was essentially the same as the previous runs using air but in this set oxygen was bubbled through the reactor. The experimental setup was the same as that with air shown in Fig. 5 except that the air supply was disconnected at the rotameter intake and a connection was made to an oxygen cylinder. Except for this minor change in the experimental setup the procedure followed in making the experiment remained essentially the same. In these runs a 2-in. diameter disc was used and the ammonia concentration was 0.5 N. A trial run was first made to determine the change in ammonia concentration when the saturators were each filled with 1 l. of 0.5 N ammonia and to determine the change in concentration of oxygen. The ammonia level was maintainable for at least 3 hr.
and the oxygen concentration reached an equilibrium value after 1 hr. For subsequent runs the stabilization time from 1 to 1 1/2 hr. Each run lasted for 30 min. and samples were taken every 10 min. The angular velocity was measured at 5, 15, and 25 min. from the start of the run. Oxygen concentration was checked between samplings during the first actual run. Replicates were also made where only the final solutions were analyzed for their copper content. The results of these runs are shown in Fig. 16. Fig. 17 shows the variation of dissolution rate with the square root of angular velocity. Increasing the oxygen concentration in solution from 8 ppm to 40 ppm nearly quadrupled the copper dissolution rate. This is illustrated in Fig. 17 where at a constant value of angular velocity the dissolution rate with pure oxygen is about four times that with air. In the preceding runs where air was used and the ammonia concentration was raised from 0.5 to 1.0 N, the copper dissolution rate remained the same. This is another indication that it was the transport of oxygen that controlled the reaction.

The next set of experiments were intended to test whether the limiting effect of oxygen diffusion could be eliminated. With 0.5 N ammonia the angular velocity was raised to more than 1700 rpm. As mentioned in the section on testing and development, laminar conditions could exist with a 2-in. disc up to a Reynolds number of about 400 rpm. This would correspond to $\omega^{1/2} = 20$. The runs beyond the laminar regime were for 10 min.
Fig. 16. Dissolution of 2-in. diameter copper disc in 2 l. of oxygen-saturated solution of 0.5 N aqueous ammonia. Solution temperature = 24°C; oxygen in solution = 40 ppm
Fig. 17. Variation of dissolution rate with square root of angular velocity for 0.5 N aqueous ammonia, oxygen- and air-saturated solutions. Solution temperature = 24°C
Both air and oxygen were used. A summary of the results obtained is included in Tables 4 and 6. The dissolution rates calculated from the results showed that increasing the angular velocity to more than 1700 rpm did not eliminate mass transfer control. A combined plot of these runs together with the previous runs with air-saturated and oxygen saturated solutions in the laminar region is shown in Fig. 18.

It would appear that the dissolution rate of copper was limited by the rate by which oxygen diffused from the bulk of the solution to the disc surface because ammonia was present in excess and, conversely, oxygen was present in relatively small quantities. Decreasing the ammonia concentration would then probably shift the control from oxygen concentration to ammonia concentration. In the next set of runs, the ammonia concentration was decreased to 0.1 and 0.05 N and oxygen was bubbled through the reactor. With 0.1 N ammonia the runs were for 30 min. In these runs 0.1 N ammonia could be maintained in the reactor for at least 2 hr. when the ammonia saturators were each filled with 1 l. of 0.1 N ammonia. The equilibrium oxygen concentration was attained in 1 hr. The stabilization time for actual runs was 1 hr. Samples were obtained every 10 min. and the angular velocity was measured between samplings. With 0.05 N ammonia the runs were for 1 hr. Samples were taken every 10 min. and the angular velocity measured between samplings. The 0.05 N ammonia in each of the ammonia saturators
Table 6. Summary of data for runs using oxygen. Oxygen in solution = 40 ppm. Initial copper in solution = 0, solution temperature = 24°C, disc diameter = 2 in.

<table>
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<tr>
<th>Run</th>
<th>NH₃ normality</th>
<th>Length of run, min.</th>
<th>Cu conc. at end of run, ppm</th>
<th>(Angular velocity, rpm)(^{1/2})</th>
<th>Dissolution rate (j_{\text{Cu}} \times 10^7) g. Cu/(sq. cm.)/(sec.)</th>
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<td>0.934</td>
</tr>
<tr>
<td>129-12</td>
<td>0.05</td>
<td>60</td>
<td>3.75</td>
<td>34.3</td>
<td>0.934</td>
</tr>
<tr>
<td>134</td>
<td>0.05</td>
<td>60</td>
<td>4.45</td>
<td>41.7</td>
<td>1.19</td>
</tr>
</tbody>
</table>

*Disc no. 2.
Fig. 18. Combined plot of dissolution rate vs. square root of angular velocity for air- and oxygen-saturated solution of 0.5 and 1.0 N aqueous ammonia including rates beyond laminar regime. Solution temperature = 24°C
maintained the ammonia concentration in the reactor for at least 2 hr. The stabilization time of 1 hr. allowed the reactor solution to attain its equilibrium oxygen concentration. Decreasing the ammonia concentration to 0.1 N and 0.05 N showed a tendency for the dissolution rate to level off to a constant value depending on the concentration of ammonia. These results are shown in Figs. 19, 20 and 21. In the bottom two lines of Fig. 19, deposits were observed on the disc at the end of the run which possibly hindered the dissolution of copper especially towards the end of the run. In the lower three lines in Fig. 20 deposits were also observed at the end of the run but not as thick as those in the bottom two lines of Fig. 19. The relatively thinner deposits in the case with the 0.05 N ammonia solutions apparently did not hinder the dissolution rate significantly. Most of the other points on Figs. 19 and 20 do not fall on straight lines. This was probably because the surface reaction was controlling at these conditions. The dissolution rates obtained by determining the slopes of these plots were approximations of the average dissolution rates for the duration of the runs. These dissolution rates are plotted in Fig. 21. Within the laminar range ($\omega^{1/2}$ below 20) the nature of the plot seemed to be of the same nature as Fig. 4. Fig. 4 is an illustration of the intermediate kinetics discussed in the section on theory. This was particularly more obvious in the runs with 0.05 N ammonia where the dissolution rate
Fig. 19. Dissolution of 2-in. diameter copper disc in 2 l. of oxygen-saturated solution of 0.1 N aqueous ammonia. Solution temperature = 24°C; oxygen in solution = 40 ppm.
Fig. 20. Dissolution of 2-in. diameter copper disc in 2 l. of oxygen-saturated solution of 0.05 N aqueous ammonia. Solution temperature = 24°C; oxygen in solution = 40 ppm
Fig. 21. Variation of dissolution rate with square root of angular velocity for 0.1 and 0.05 N aqueous ammonia, oxygen-saturated solution. Solution temperature = 24°C; 2-in. diameter disc
appeared to increase linearly with $\omega^{1/2}$ at low angular velocities and levelled off to about a constant value at about $\omega^{1/2} = 20$. This type of plot indicates a transition from the diffusion controlled regime to the surface reaction-controlled regime. This set of experiments indicated that the ammonia concentration may be limiting at ammonia concentrations of 0.1 N and below. This is related to Halpern's (16) findings that at high oxygen concentrations the dissolution rate is dependent on ammonia concentration. The relative magnitudes of ammonia and oxygen concentrations thus seem to determine whether diffusion of oxygen or surface reaction and concentration of ammonia are rate limiting.

The bulk of this experimental investigation was made with 0.5 N ammonia solutions and with an oxygen concentration which did not exceed 40 ppm. In this region the dissolution rate was determined by the rate at which oxygen diffused from the bulk of the solution to the surface of the copper disc.

Solution saturated with oxygen-nitrogen mixture

Although the dissolution rate of copper in aqueous ammonia was found to be controlled by the diffusion of oxygen, it was not clear why the dissolution rate increased by only four times when the oxygen in solution was increased from 8 ppm to 40 ppm. According to Equation 43 the increase should be fivefold instead of four. The lower value of dissolution rate than what was expected could be attributed to a decrease in the
diffusivity of oxygen at higher concentrations. An experiment similar to the previous runs but where the concentration of oxygen was between 8 ppm and 40 ppm could give additional information on this regard. The gas mixture was prepared in a tank and connected to the reaction system. The tank was first evacuated by suction with an aspirator, filled with nitrogen to about 40 psig, and then with oxygen to about 100 psig. The tank was connected to the pressure regulator shown in Fig. 5 and the gas mixture was admitted into the system as in the case with air. Stabilization time was for 30 min. Samples were withdrawn every 10 min. and the solution temperature, oxygen concentration, and angular velocity were measured between samplings. Table 7 summarizes the data for this run. The average oxygen concentration was 22.7 ppm and the average angular velocity was 333 rpm. Fig. 22 graphically illustrates the result of this run. The dissolution rate was determined from the slope of the line in Fig. 22 and amounted to $10.72 \times 10^{-7}$ g. Cu/(sq. cm.)(sec.). From Fig. 17 the copper dissolution rates corresponding to an angular velocity of 333 rpm or to a square root of angular velocity which is 18.23 are $3.75 \times 10^{-7}$ and $15.3 \times 10^{-7}$ g. Cu/(sq. cm.)(sec.) for air-saturated solutions and oxygen-saturated solutions, respectively. Dissolution rates at 333 rpm can therefore be plotted against concentration of oxygen in solution as in Fig. 23. The plot shows a first order relationship between dissolution rate and
Fig. 22. Dissolution of 2-in. diameter copper disc in 2 l. of 0.5 N aqueous ammonia with oxygen concentration at 22.7 ppm. Solution temperature = 24°C. Run 191
Fig. 23. Variation of dissolution rate with oxygen concentration at constant angular velocity. 0.5 N aqueous ammonia; 2-in. diameter disc; solution temperature = 24°C
Table 7. Data for run with oxygen-nitrogen mixture. Disc diameter = 2 in.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Temp. (°C)</th>
<th>O₂ Conc. (ppm)</th>
<th>Ang. vel. (rpm)</th>
<th>Cu. conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24</td>
<td>22.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>24</td>
<td></td>
<td>340</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>24</td>
<td>22.7</td>
<td></td>
<td>6.4</td>
</tr>
<tr>
<td>15</td>
<td>24</td>
<td>22.7</td>
<td>338</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>24</td>
<td>22.7</td>
<td></td>
<td>13.0</td>
</tr>
<tr>
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<td>22.7</td>
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</tr>
<tr>
<td>35</td>
<td>24</td>
<td>22.7</td>
<td>323</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>24</td>
<td>22.7</td>
<td></td>
<td>25.6</td>
</tr>
<tr>
<td>45</td>
<td>24</td>
<td>22.9</td>
<td>336</td>
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<td>32.8</td>
</tr>
<tr>
<td>55</td>
<td>24</td>
<td>22.8</td>
<td>333</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>24</td>
<td></td>
<td></td>
<td>39.2</td>
</tr>
</tbody>
</table>

oxygen concentration in solution up to about 20 ppm oxygen. The constants in Equation 43 are unchanged within this range. Deviation from linearity from about 20 ppm to 40 ppm oxygen in solution may be attributed to a change in diffusivity of oxygen at higher oxygen concentrations.
Dissolution with cupric ammine complex

There had been evidence from the work of Yamasaki (36), Vora (32), and Wu (35) that the dissolution of copper in aqueous ammonia is autocatalytic. It was then desirable to isolate the dissolution of copper by the cupric ammine complex from the dissolution by oxygen in the solution. The series of experiments using pre-purified nitrogen in place of air or oxygen was intended to study the dissolution of copper by the cupric ammine complex separately. One of the first concerns was to eliminate the oxygen in the reactor solution or else reduce it to the point where its concentration was not sufficient to cause a significant rate of dissolution of copper. Two runs were made where the ammonia concentration in the solution was 0.523 N and without any copper initially present in solution. The nitrogen was bubbled through the reactor for 1 hr. before making the run. In the first run, run 148, a 2-in. diameter disc was spinning in the solution at 316 rpm. The oxygen concentration was determined every 10 min. and the first three readings were 0.25 ppm. The last three readings in the 1-hr. run were 0.20 ppm. Samples of the initial and final solution were analyzed for copper content and the final solution contained not more than 0.05 ppm copper. The second run, run 149, was like run 148 and a 2-in. disc was spinning at 338 rpm. The oxygen concentration in solution at the start and at the middle of the run was 0.15 ppm. The samples from the original and final solution were also analyzed for their
copper content and both samples did not show any trace of copper present. These runs demonstrated that the oxygen could be driven out of the system to the point where its presence was insignificant.

The runs isolating the dissolution of copper by the cupric ammine complex could therefore be made. The dissolution of a 2-in. diameter disc in 0.5 N aqueous ammonia containing 50, 200, and 500 ppm copper as the cupric ammine complex initially in the solution was investigated. The experimental conditions are summarized in Table 8. The preparation of these solutions is described under the section on procedures. The runs were for 1 hr. with a stabilization time of 1 hr. Samples were taken at the end of the runs and were analyzed for their copper content as were also the initial solutions. The dissolution rate for each run was calculated by assuming the rate to be constant over the entire run. No experiments were carried out to verify whether rate was constant with time. The results of these experiments are shown in Fig. 24. The dissolution rates obtained with 200 ppm copper were four times those with 50 ppm copper initially in the solution for the same angular velocity. However, the rates obtained with 500 ppm copper were about the same as those with 200 ppm copper. There was one noticeable difference though. The copper surface was uniform and clean at the end of the run when the starting solution was either 50 or 200 ppm copper. With 500 ppm copper the copper surface was
Table 8. Summary of data for dissolution with cupric ammine complex. Oxygen in solution = 0. Solution temperature = 24°C. Disc diameter = 2 in. All runs for 1 hr.

<table>
<thead>
<tr>
<th>Run</th>
<th>$c_i$, initial Cu conc., ppm</th>
<th>$c_f$, final Cu conc., ppm</th>
<th>$c_{o} = c_i - \frac{(c_f - c_i)}{2}$</th>
<th>Ave. NH$_3$ normality</th>
</tr>
</thead>
<tbody>
<tr>
<td>148</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.524</td>
</tr>
<tr>
<td>149</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.523</td>
</tr>
<tr>
<td>143</td>
<td>52.5</td>
<td>58.5</td>
<td>49.5</td>
<td>0.547</td>
</tr>
<tr>
<td>147</td>
<td>53.0</td>
<td>59.0</td>
<td>50.0</td>
<td>0.516</td>
</tr>
<tr>
<td>163</td>
<td>51.5</td>
<td>54.5</td>
<td>50.0</td>
<td>0.524</td>
</tr>
<tr>
<td>166</td>
<td>46.0</td>
<td>50.0</td>
<td>44.0</td>
<td>2.00</td>
</tr>
<tr>
<td>167</td>
<td>47.0</td>
<td>53.0</td>
<td>44.0</td>
<td>1.96</td>
</tr>
<tr>
<td>159</td>
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<td>525</td>
<td></td>
<td>0.515</td>
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</tr>
<tr>
<td>170</td>
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<td></td>
<td>0.529</td>
</tr>
<tr>
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<td>500</td>
<td>525</td>
<td></td>
<td>0.522</td>
</tr>
<tr>
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<td>218</td>
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<td>0.550</td>
</tr>
<tr>
<td>168</td>
<td>200</td>
<td>210</td>
<td>195</td>
<td>0.517</td>
</tr>
<tr>
<td>169</td>
<td>200</td>
<td>206</td>
<td>197</td>
<td>0.521</td>
</tr>
<tr>
<td>171</td>
<td>202</td>
<td>218</td>
<td>194</td>
<td>0.524$^b$</td>
</tr>
<tr>
<td>176</td>
<td>218</td>
<td>236</td>
<td>209</td>
<td>0.710$^b$</td>
</tr>
<tr>
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<td>232</td>
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</tr>
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<td>210</td>
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<tr>
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<td>230</td>
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<tr>
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<td>204</td>
<td>220</td>
<td>196</td>
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</tr>
<tr>
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</tr>
<tr>
<td>179</td>
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<td>485</td>
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</tr>
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<tr>
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</tr>
<tr>
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<td>510</td>
<td>540</td>
<td>495</td>
<td>0.525$^c$</td>
</tr>
<tr>
<td>188</td>
<td>560</td>
<td>600</td>
<td>540</td>
<td>1.273$^d$</td>
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<tr>
<td>190</td>
<td>475</td>
<td>505</td>
<td>460</td>
<td>0.525$^c$</td>
</tr>
</tbody>
</table>

$^a$Disc no. 2.

$^b$Total NH$_3$: solution prepared as 0.525 N NH$_3$.

$^c$Solution prepared as 0.525 N NH$_3$. Total NH$_3$ unchecked.

$^d$Solution prepared as 1.273 N NH$_3$. Total NH$_3$ unchecked.
<table>
<thead>
<tr>
<th>(NH₄)₂CO₃ molarity</th>
<th>Angular velocity, rpm</th>
<th>$\sqrt{c_0 \times 10^3}$</th>
<th>$j_{cu} \times 10^7$ g. Cu/(sq. cm.)(sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>0</td>
<td>0</td>
</tr>
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<td>0</td>
<td>18.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<tr>
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</tr>
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<td>2.75</td>
</tr>
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<td>7.78</td>
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<tr>
<td>1.95</td>
<td>18.5</td>
<td>8.51</td>
<td>8.24</td>
</tr>
</tbody>
</table>
Fig. 24. Dissolution of copper by the cupric ammine complex at various ammonia and ammonium carbonate concentrations. Nitrogen-saturated solutions (= 0 oxygen); solution temperature = 24°C; 2-in. diameter disc
covered by a thin deposit. At an angular velocity of 69 rpm (run 162) very slight brownish streaks were observed. At angular velocities of 171 to 378 rpm (runs 159 to 161, 170, 172) there appeared to be a more uniformly spread deposit that had a gray-yellow-green tint. These deposits were probably of the same kind that Yamasaki (36) observed and were thought to be anhydrous cupric oxide or precipitated cupric hydroxide or possibly a combination of both. When the reactor solution was made 0.1 M with respect to ammonium carbonate, the copper surface remained clean and free of deposits even with 500 ppm copper in the starting solution. The dissolution rate at a constant angular velocity also increased to about 10 times that with 50 ppm copper.

It was evident that in the absence of oxygen but in the presence of the cupric ammine complex, copper was oxidized and went into solution according to

$$\text{Cu} + \text{Cu(NH}_3\text{)}_4^{2+} + x\text{NH}_3 = 2 \text{Cu(NH}_3\text{)}^{4+x}_2$$

and the dependency of the dissolution rate on angular velocity indicated that the reaction was also diffusion controlled. This is analogous to the case when the copper was oxidized by oxygen. If the dissolution rate was controlled by the diffusion of the cupric ammine complex, the rate should be given by Equation 43 where $c_0$ and $D$ now refer to the cupric ammine complex instead of oxygen. The proportionate increase of
dissolution rate with the concentration of cupric ammine complex in solution provided additional evidence that the diffusion of cupric ammine complex from the bulk of the solution to the surface of the disc was the controlling factor in this reaction. A better way to look at the data would be to plot the product of the square root of angular velocity and the cupric ammine concentration against dissolution rate. In the experiment being considered here the concentration of the cupric ammine complex could not be maintained constant as in the case of the previous experiments with oxygen so that grouping the square root of angular velocity with the concentration should produce a linear plot with all the data falling on the same line providing the rate was diffusion controlled. This appeared to be nearly the case as can be seen from Fig. 25. For this plot an average concentration of the cupric ammine complex was employed. It was assumed that the concentration of the cupric ammine complex decreased during any given run by the amount which the total concentration of copper in solution increased. In other words, it was assumed that the oxygen in solution was insufficient to reoxidize the cuprous copper.

Inasmuch as ammonia was still a reactant in the dissolution of copper by the cupric ammine complex, the effect of increasing its concentration on copper dissolution rate was investigated. The ammonia concentration was raised from 0.5 to 2 N in runs
Fig. 25. Variation of dissolution rate with $(rpm)^{1/2}(c_0)$ where $c_0$ is the average concentration of cupric ammine complex in solution. Dissolution with cupric ammine complex
166 and 167 where the initial copper in solution was approximately 50 ppm. The increase in ammonia concentration did not affect the dissolution as shown in Fig. 24 and this eliminated the possibility that the transport of ammonia limited the dissolution rate.

Addition of more ammonium carbonate to concentrations of 0.5 M and above seemed to decrease the dissolution rate. Although the runs with 0.1 M ammonium carbonate prevented the formation of deposits on the copper surface thus enabling the dissolution rate to proceed as first order with respect to cupric ammine concentration, increasing the ammonium carbonate in solution beyond that which was required to keep the copper surface clean apparently decreased the dissolution rate. This is illustrated by the data in Figs. 24 and 25 and also Table 8. Run 183 with 0.5 M ammonium carbonate and runs 186 and 188 with 0.6 M ammonium carbonate fell below their respective lines in Fig. 24 and below the composite plot in Fig. 25. The decrease in dissolution rate with 1.95 M ammonium carbonate as in run 190 was even greater. One possible explanation to the decrease in reaction rate corresponding to an increase in ammonium carbonate concentration was an increase in the viscosity of the solution. The viscosity term enters as $v^{-1/6}$ in the convective diffusion equation, Equation 43. The viscosity of the solution used in this section was therefore
measured using an Ostwald viscosimeter (28). The results of these measurements are summarized in Table 9. Water whose kinematic viscosity at 20°C is 0.01 sq. cm./sec. (33) was used as reference liquid. Since the change in the sixth root of kinematic viscosity was small, the decrease in dissolution rate as described by Equation 43 could not be fully accounted for by the increase in kinematic viscosity of the solution as the ammonium carbonate concentration was increased. The decrease in dissolution rate due to the addition of more ammonium carbonate beyond what was required to keep the copper surface clean may be due to three possible reasons: (a) the addition of excess ammonium carbonate binds the cupric ammine complex to the carbonate ion, thus reducing the concentration of free cupric ammine, i.e.,

$$\text{Cu(NH}_3\text{)}_4^{++} + \text{CO}_3^{=} = \text{Cu(NH}_3\text{)}_4\text{CO}_3$$

-addition of more $\text{CO}_3^{=}$ shifts the above equilibrium reaction to the right, (b) the presence of excess ammonium carbonate reduces the diffusivity of the cupric ammine complex, and (c) a combination of a and b.

The diffusivity of the cupric ammine complex was obtained by using Equation 43 and Fig. 25. The dissolution rate of copper in this case was equal to the rate by which the cupric ammine ion was transported from the bulk of the solution to the surface of the disc by virtue of the stoichiometry in Equation 58. The slope of the graph in Fig. 25 is equal to the ratio of
Table 9. Kinematic viscosity of reactor solutions

<table>
<thead>
<tr>
<th>Solution&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Run</th>
<th>( \nu ), sq. cm./sec.</th>
<th>( \nu^{+1/6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ppm Cu</td>
<td>165</td>
<td>1.018</td>
<td>1.003</td>
</tr>
<tr>
<td>200 ppm Cu</td>
<td>165</td>
<td>1.022</td>
<td>1.003</td>
</tr>
<tr>
<td>500 ppm Cu</td>
<td>165</td>
<td>1.021</td>
<td>1.003</td>
</tr>
<tr>
<td>0.1 M(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>193</td>
<td>1.046</td>
<td>1.008</td>
</tr>
<tr>
<td>200 ppm Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 M(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>193</td>
<td>1.115</td>
<td>1.018</td>
</tr>
<tr>
<td>200 ppm Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>193</td>
<td>1.033</td>
<td>1.005</td>
</tr>
<tr>
<td>500 ppm Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6 M(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>187</td>
<td>1.130</td>
<td>1.020</td>
</tr>
<tr>
<td>500 ppm Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.95 M(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>193</td>
<td>1.448</td>
<td>1.063</td>
</tr>
</tbody>
</table>

<sup>a</sup>All solutions 0.5 N in ammonia.

mass flux of cupric ammine to \( \omega^{1/2} \) \( c_o \). Using \( \nu = 1.003 \) sq. cm./sec. from Table 9, the diffusivity of the cupric ammine complex was \( 8.93 \times 10^{-7} \) sq. cm./sec. by Equation 43.

Dissolution with oxygen and cupric ammine complex

It was apparent that the dissolution rate of copper in aqueous ammonia was determined by either the transport of oxygen or the cupric ammine ion from the bulk of the solution to the
surface of the copper disc. Run 189 was made to test whether the reactions were additive as suggested by Yamasaki (36). As initial reactor solution, 2200 ml. of 0.5 N ammonia containing approximately 50 ppm copper was prepared. The solution was air-saturated and at the end of the 1-hr. run samples of the initial and final solutions were analyzed for their copper content. The data for run 189 is summarized in the following table:

Table 10. Summary of data for run 189. Disc diam. = 2 in.; 0.5 N NH₃

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>°C</td>
<td>ppm</td>
<td>rpm</td>
<td>ppm</td>
</tr>
<tr>
<td>0</td>
<td>24</td>
<td>8.25</td>
<td></td>
<td>52.5</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>360</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
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<td>355</td>
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<td>25</td>
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<td>351</td>
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<td>35</td>
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<td></td>
<td>354</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td></td>
<td></td>
<td>332</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td></td>
<td></td>
<td>335</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>24</td>
<td>8.3</td>
<td></td>
<td>74.0</td>
</tr>
</tbody>
</table>
The 21.5 ppm increase of copper in solution in 1 hr. corresponded to a dissolution rate of $5.92 \times 10^{-7}$ g. Cu/(sq. cm.) (sec.). The average angular velocity was 347 rpm. From Fig. 17 the copper dissolution rate corresponding to an $(\text{rpm})^{1/2}$ of 18.63 is $3.85 \times 10^{-7}$ g. Cu/(sq. cm.)(sec.) for an air-saturated solution with zero initial copper. From Fig. 24 and also Table 8, the copper dissolution rate corresponding to an average cupric ammine concentration of 50 ppm is $1.65 \times 10^{-7}$ g. Cu/(sq. cm.)(sec.). The last value was when oxygen was not present in the solution, so that

$$j_{\text{Cu}} = K_2 c_{\text{Cu}}$$

$$K_2 = \frac{1.65 \times 10^{-7}}{50}.$$

The dissolution rate corresponding to an average cupric ammine ion concentration of 63.2 ppm was

$$j_{\text{Cu}} = \left(\frac{1.65 \times 10^{-7}}{50}\right) (63.2) = 2.08 \times 10^{-7} \text{ g. Cu/(sq. cm.) (sec.).}$$

When this was added to $3.85 \times 10^{-7}$, the total copper dissolution rate was $5.93 \times 10^{-7}$ g. Cu/(sq. cm.)(sec.). This was almost the same as $5.92 \times 10^{-7}$ g. Cu/(sq. cm.)(sec.) obtained from run 189.

Apparently the dissolution of copper in aqueous ammonia can therefore be described by the following equation:
\[ j_{\text{Cu}} = K_1 C_{O_2} + K_2 C_{\text{Cu}} \]  \hspace{1cm} (59)

where \( j_{\text{Cu}} \) is the copper dissolution rate; \( K_1 \) and \( K_2 \) are constants; \( C_{O_2} \) is the concentration of oxygen in solution and \( C_{\text{Cu}} \) is the concentration of the cupric ammine complex in solution. The constants \( K_1 \) and \( K_2 \) are proportional to the terms \( D^{2/3} \nu^{-1/6} \omega^{1/2} \) of Equation 43. Therefore, \( K_1 \) and \( K_2 \) are constants only at constant angular velocity, kinematic viscosity, and diffusivity. It is not known to what range of values of oxygen and copper concentrations Equation 59 is applicable. The result of run 189 which was applicable to Equation 59 was only for an oxygen concentration of about 8 ppm and an average cupric ammine concentration of 63.2 ppm.

Equation 59 is similar to Equation 1 proposed by Yamasaki (36) but Equation 59 describes the dissolution rate as first order with respect to both oxygen and cupric ammine complex concentrations. The first order nature of copper dissolution with respect to oxygen and copper results from the nature of the reaction which is one that is diffusion-controlled. Equation 59 is actually an extension of Equation 43 which is the theoretical equation for the limiting mass flux of a reactant whose transport from the bulk of the solution to the surface of a rotating disc is controlling. Yamasaki (36) hinted on the possibility of a diffusion-controlled reaction but excluded this concept by virtue of the non-first-order
relationship of dissolution rate with oxygen concentration which he obtained. This report, however, shows the first-order nature of copper dissolution with respect to oxygen concentration. The actual oxygen concentrations in solution which were measured rather than assumed and the nature of the results which parallel what would be predicted by the theoretical convective diffusion equation support this observation. There is ample evidence not only from this work but from that of Yamasaki (36), Vora (32) and Wu (35) about the autocatalytic nature of copper dissolution in aqueous ammonia to disprove Lane and McDonald's (19) claim that it is not. The bulk of Halpern's work (16) was purposely beyond the region where oxygen concentration and angular velocity affected the dissolution and was accomplished by working with oxygen pressures well above one atmosphere.

**Dissolution of copper wire in a bubble reactor**

The runs with the bubble reactor was designed to approximate the conditions in run W-69-NR-6 by Wu (35). These runs measured the dissolution rate of a measured length of wire suspended in a solution of 0.5 N ammonia and 0.1 M ammonium carbonate. The procedure for this experiment is discussed in the section on procedures. Run 155 whose results are shown in Fig. 26 was made with a copper wire 57 1/8 in. long and with a solution volume of 220 ml. The dissolution rates were calculated by taking slopes of the concentration curve midway
Fig. 26. Dissolution of copper wire (surface area = 46.8 cm sq. cm.) in bubble reactor. Solution is 220 ml. of 0.5 N ammonia and 0.1 M ammonium carbonate. Run 155.
between sampling points. For example, to get the dissolution rate midway between the 15- and 30-min. periods, the points joining the concentration at 15 min. and the concentration at 30 min. were connected. The slope of the connecting line was multiplied by the volume of the solution and divided by the surface area of the copper wire which was 46.8 sq. cm. to give the dissolution rate at 22 1/2 min. This run confirmed the autocatalytic nature of copper dissolution pointed out by Yamasaki (36). The dissolution rate went up to a maximum after which the dissolution rate dropped when presumably deposits formed on the copper surface. Inspection of the copper wire at the end of the run, however, showed that the wire looked clean. It was quite possible though that these deposits were more difficult to observe due to the thinness of the wire. The deposits on the disc surface mentioned previously were more prominent since the large, even area was more easily detectable for variations in color and texture. Inspecting the wire through a microscope immediately after the run would have given a better information on the nature of the copper surface. It was more likely, however, that the decrease in dissolution rate was due to a drastic decrease in ammonia concentration. Although the blank run showed no change in ammonia concentration after 2 1/2 hr., this was true only when no copper was present in the solution. From Fig. 26, the copper concentration at the maximum dissolution rate was about 7 g./l.. This would correspond to 0.11 mole/l. of copper. If this copper were in
the cupric tetramine form, 0.44 mole/l. of ammonia would be needed. The original ammonia concentration was only 0.5 N and ammonium carbonate was 0.1 M giving a total ammonia concentration of 0.70 mole/l. Even if the total ammonia were considered, only 0.26 mole/l. would remain available at the maximum dissolution rate. It was observed in the previous runs that at low ammonia concentrations (0.1 N and below), the ammonia concentration was rate limiting due to the shift from a diffusion controlled reaction determined by the transport of oxygen from the bulk of the solution to the surface of the copper disc, to a surface controlled reaction limited by the concentration of ammonia. Another oxidizing agent was present in the bubble reactor which was the cupric ammine complex. Thus, the overall reaction rate would most likely be shifted earlier from a diffusion controlled reaction to a surface controlled reaction determined by the concentration of ammonia. The dissolution rate continued to drop as the concentration of ammonia further declined. The final copper concentration measured was 11.5 g./l. or 0.181 mole/l. If this copper were in the cupric tetramine form, 0.724 mole/l. ammonia would be needed which was more than the total ammonia present. Towards the end of the run, therefore, some of the copper was associated with less than four ammonia molecules.

Temperature measurements with the bubble reactor run showed that the temperature rose in the region where the
dissolution rate rose rapidly. Oxygen concentration dropped slightly in this region. Oxygen readings were not steady from about 45 to 90 min. from the start of the dissolution but ranged from 6.8 to 7.4 ppm. The oxygen concentration then rose steadily to 8.0 ppm towards the end of the 2-hr. run. The decrease in oxygen concentration may have been due partly to a decrease in oxygen solubility as a result of the increase in temperature or partly due to the inability of the system to replace the oxygen as fast as it was reacted.
CONCLUSIONS

The following conclusions were derived from this investigation involving the dissolution of copper in aqueous ammonia:

1. Copper can be dissolved by either oxygen or the cupric ammine complex. This is a confirmation of Yamasaki's findings.

2. The dissolution rate is first order with respect to oxygen rather than half-order as suggested by Yamasaki. It is also first order with respect to the cupric ammine complex as observed by Yamasaki.

3. Copper dissolution is diffusion-controlled. It is limited by the transport of oxygen and/or of cupric ammine complex from the bulk of the solution to the surface of the metal.

4. The dissolution rates of copper by oxygen and by the copper ammine complex are additive.

5. With ammonia concentrations of 0.1 N and below and oxygen concentration of at least 40 ppm, the rate of copper dissolution may be limited by the concentration of ammonia.

6. With high concentrations of copper in solution (above 200 ppm), deposits on the copper surface inhibit the dissolution of copper and cause the rate to be less than that predicted by Equation 59. Addition of ammonium carbonate prevents the formation of these deposits and makes Equation
59 applicable.

7. Addition of more ammonium carbonate beyond that which is required to prevent deposits to form on the copper surface seems to decrease the dissolution rate. This may be due to three possibilities: (a) excess ammonium carbonate decreases the concentration of free cupric ammine complex; (b) more ammonium carbonate decreases the diffusivity of cupric ammine complex, and (c) combination of a and b.

8. The diffusivity of oxygen in 0.5 N aqueous ammonia is \[5.57 \times 10^{-5}\] sq. cm./sec.

9. The diffusivity of cupric ammine complex in 0.5 N aqueous ammonia is \[8.93 \times 10^{-7}\] sq. cm./sec.
LITERATURE CITED


NOMENCLATURE

A constant

$a_1$ constant of integration

$a_2$ constant of integration

B constant

c number of dissolved particles per unit volume of liquid, ppm or mole/l.

c_{1,2,3} constants

c_o value of c in the bulk of the solution, ppm or mole/l.

c_{cu} concentration of copper in solution, ppm or mole/l.

c_{o2} concentration of oxygen in solution, ppm or mole/l.

c_s value of c at surface of disc, ppm or mole/l.

D diffusion coefficient, L^2/t

F function of δ used in casting $V_r$ into dimensionless form

$F_0, F_1, F_2, F_3$ constant coefficients in series expansion of F for large values of δ

f volume force, L/t^2

$f_o, f_1, f_2, f_3$ constant coefficients in series expansion of F for small values of δ

G function of δ used in casting $V_\theta$ into dimensionless form

H function of δ used in casting $V_y$ into dimensionless form

I $I_1 + I_2$
\[ I_1 \int_0^e \exp \left( \frac{1}{D} \int_0^t V_y \, dz \right) \, dt \]

\[ I_2 \int_\infty^0 \exp \left( \frac{1}{D} \int_0^t V_y \, dz \right) \, dt \]

\[ j \quad \text{total flux of matter, sum of } j_d \text{ and } j_{\text{conv}} \quad \text{g.}/(\text{sq. cm.})(\text{sec.}) \]

\[ j_d \quad \text{flux of matter due to molecular diffusion, } \text{g.}/(\text{sq. cm.})(\text{sec.}) \]

\[ j_{\text{conv}} \quad \text{flux of matter due to velocity of fluid, } \text{g.}/(\text{sq. cm.})(\text{sec.}) \]

\[ j_{\text{cu}} \quad \text{dissolution rate of copper, } \text{g. Cu}/(\text{sq. cm.})(\text{sec.}) \]

\[ j_0 \quad \text{mass flux of oxygen, } \text{g.}/(\text{sq. cm.})(\text{sec.}) \]

\[ k \quad \text{reaction rate constant} \]

\[ K_1 \quad \text{constant} \]

\[ K_2 \quad \text{constant} \]

\[ m \quad \text{reaction order} \]

\[ n \quad \text{positive unit normal to } S \]

\[ p \quad \text{function of } \delta \text{ used in casting } p \text{ into dimensionless form} \]

\[ p \quad \text{fluid pressure, } \text{M}/\text{Lt}^2 \]

\[ Q \quad \text{number of particles passing through } S \text{ in one second} \]

\[ r \quad \text{radial distance in cylindrical coordinate system, } L \]

\[ S \quad \text{surface area of } V_0, L^2 \]

\[ t \quad \text{dimensionless concentration, } c_S/c_0 \]
\( V \) velocity of fluid, \( L/t \)
\( V_0 \) an arbitrary volume of fluid
\( x \) coordinate in space, \( L \)
\( y \) coordinate in space, \( L \)
\( z \) coordinate in space, \( L \)
\( \omega \) angular velocity, \( \text{rad}/t \)
\( \rho \) fluid density, \( M/L^3 \)
\( \mu \) viscosity, \( M/Lt \)
\( \theta \) angle in cylindrical coordinate system, \( \text{rad} \)
\( \nu \) kinematic viscosity, \( \mu/\rho, L^2/t \)
\( \delta \) dimensionless quantity, \( \left( \frac{\omega}{\nu} \right)^{1/2} \)
\( \beta \) constant, \( \frac{x}{(\nu \omega)^{1/2}} \)
\( \varepsilon_0 \) hydrodynamic boundary layer thickness, \( L \)
\( \varepsilon \) diffusion boundary layer thickness, \( L \)
\( \overline{\cdot} \) overline to denote vector quantity
\( ' \) superscript to denote first derivative with respect to \( \delta \)
\( '' \) superscript to denote second derivative with respect to \( \delta \)
ACKNOWLEDGEMENTS

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Statistical Analysis for Slopes in Figs. 12 and 15

Model:

\[
Y = \beta X + X\varepsilon
\]

where \(\varepsilon = N(0,\sigma)\)

\[
\frac{Y}{X} = \beta + \varepsilon
\]

\[
\bar{Y} = \frac{Y}{X}
\]

\[
s^2 = \frac{\sum \left(\frac{Y}{X}\right) - \left(\frac{Y}{X}\right)^2}{n - 1}
\]

Confidence interval for \(\beta_1 - \beta_2\)

\[
\beta_1 - \beta_2 = (\bar{Y}_1 - \bar{Y}_2) + t' \left( \sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}} \right)
\]

where

\[
t' = \left[ \frac{\frac{s_1^2}{n_1}}{\frac{s_2^2}{n_2}} \right] t_{(n_1-1)} + \left[ \frac{s_2^2}{n_2} \right] t_{(n_2-1)}
\]

Let

\[
\beta_1 = \text{slope for 0.5 N NH}_3,\ 2\text{-in. diameter disc}
\]

\[
\beta_2 = \text{slope for 1.0 N NH}_3,\ 2\text{-in. diameter disc}
\]

\[
\beta_3 = \text{slope for 0.5 N NH}_3,\ 3\text{-in. diameter disc}
\]
C. I. for $\beta_1 - \beta_2 = (-0.00492 \text{ to } 0.02029) \times 10^{-7}$

C. I. for $\beta_1 - \beta_3 = (0.01145 \text{ to } 0.04393) \times 10^{-7}$

The following $t$ values were used:

\[
\begin{align*}
t_{0.025, n_1-1} &= t_{0.025, 9} = 2.262 \\
t_{0.025, n_2-1} &= t_{0.025, 9} = 2.262 \\
t_{0.025, n_3-1} &= t_{0.025, 3} = 3.182
\end{align*}
\]