

A mass transfer model for the autocatalytic dissolution of a rotating copper disc in oxygen saturated ammonia solutions

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A mathematical model of mass transfer processes during autocatalytic dissolution of metallic copper in oxygen-containing ammonia solutions using the rotating disc technique is presented. The model is based on the equations of steady state convective diffusion with volumetric mass generation terms and boundary conditions of the third kind, in more generalized form, at the disc surface and of the first kind in the bulk solution. The boundary value problem was solved numerically using the finite difference method with variable mesh spacing. Comparison of calculated and experimental results indicates that the model quantitatively represents the measurements. The rate of the reaction $\text{Cu(II)} + \text{Cu} \rightarrow 2\text{Cu(I)}$ determines the overall rate of the process.

Nomenclature

A	rotating disc surface area, (cm^2)
B	dimensionless constant, $B = k_3 c_1^0 \omega^{-1}$
c_i	concentration of species i , $c_i = c_i(y)$ (mol cm^{-3})
c_i^0	concentration of species i in the bulk of solution, $c_i^0 = c_i^0(t)$ (mol cm^{-3})
$c_{i,0}$	concentration of species i at the disc surface, $c_{i,0} = c_i(y=0)$ (mol cm^{-3})
C_i	concentration ratio, $C_i = c_i/c_i^0$, $C_i = C_i(\xi)$
C_i^0	concentration ratio (in the bulk of solution), $C_i = c_i^0/c_i^0$
$C_{i,0}$	concentration ratio (at the disc surface), $C_{i,0} = c_{i,0}/c_i^0$
D_i	molecular diffusivity of species i ($\text{cm}^2 \text{s}^{-1}$)
h	space increment, $h = \Delta\xi = (\omega/\nu)^{1/2} \Delta y$, dimensionless
j_i	mass flux of species i ($\text{mol cm}^{-2} \text{s}^{-1}$)
k_i	first-order reaction rate constant (cm s^{-1} or $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
$K_{i,j}$	diffusivity ratio, $K_{i,j} = D_i/D_j$, dimensionless
M	number of space increments
n_i	total number of moles of Cu(II) entering the bulk of solution referred to the unit disc surface area (mol cm^{-2})

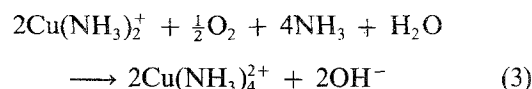
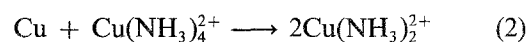
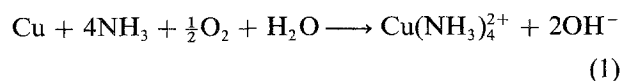
\dot{r}_i	rate of production of species i by the chemical reaction ($\text{mol cm}^{-3} \text{s}^{-1}$)
Sc_i	Schmidt number, $Sc_i = \nu_i/D_i$
t	time, (s)
Δt	time increment (s)
\mathbf{v}	fluid velocity vector $\mathbf{v} = (u, v, w)$ (cm s^{-1})
V	volume of solution (cm^3)
W_1, W_2	dimensionless group, $W_1 = (K_{3,2}/D_1)(\nu/\omega)^{1/2}$, $W_2 = (K_{1,2}/D_2)(\nu/\omega)^{1/2}$
x_l	coordinates, $l = 1, 2, 3$
y	axial coordinate (perpendicular to the disc surface)
Δy	space increment (cm)

Greek letters

∇	nabla operator
ν	kinematic viscosity of solution ($\text{cm}^2 \text{s}^{-1}$)
μ_i	stoichiometric coefficients
ω	disc angular velocity (s^{-1})
ξ	dimensionless axial coordinate, $\xi = (\omega/\nu)^{1/2} y$
$\Delta\xi$	dimensionless space increment, $\Delta\xi = (\omega/\nu)^{1/2} \Delta y$

1. Introduction

An experimental study of spontaneous copper dissolution in oxygen-containing aqueous ammonia solutions carried out by Zembura and Maraszewska [1] shows that the sequence of reactions is as follows:



Reaction 1 proceeds in the diffusion-controlled regime [1] whereas Reaction 2, particularly at high concentrations of Cu(II) complexes, is very likely to occur in the mixed regime [2]. Because of the absence of Cu(I)

complexes in the solution, Reaction 3 can be assumed to be very fast in comparison with Reaction 2. Therefore, the rate of accumulation of Cu(II) complexes in the bulk solution is the sum of the rates of Reactions 1 and 2. The substrate of Reaction 2, Cu(II), is continuously reproduced in Reaction 3, making the dissolution process autocatalytic. The main purpose of this study is to formulate and solve the mathematical model for the mass transfer processes due to the reactions described above. Making use of the rotating disc technique, the mathematical model proposed by Levich [3, 4] can be utilized as the base for more rigorous analysis.

2. Mass transfer model

Generally, the diffusion and convection mass transfer processes can be described by a set of partial differential equations:

$$\frac{\partial c_i}{\partial t} + (\mathbf{v} \cdot \nabla)c_i = \nabla(D_i \cdot \nabla c_i) + \dot{r}_i \quad (4)$$

where $c_i = c_i(x_i, t)$, ($i = 1, 2, 3$), $r_i = r_i(c_i, c_j, t)$, $D_i = D_i(c_i, c_j)$, ($i, j = 1, 2, \dots, r$), and $\mathbf{v} = (u, v, w)$. Based on the analysis of experimental data [1] the Equations 4 can be significantly simplified by assumption that the concentration of all species, i , changes very slowly with time so that $\partial c_i / \partial t = 0$. This means that the process can be considered as quasi-steady state. To simplify the problem further we assume that the Reaction 3 is first order and irreversible for dissolved oxygen and Cu(I) complexes and that these species are at low concentration in comparison with ammonia and water. Additionally, the molecular diffusivity of all species, i , in the liquid, D_i , can be assumed independent of concentration and mass transfer processes can be considered as unidimensional. Under such assumptions, based on the Levich model [3], the equations of convective diffusion take the simplified form:

$$D_i \frac{d^2 c_i}{dy^2} - v \frac{dc_i}{dy} + \mu_i k_3 c_1 c_2 = 0 \quad (\text{for } i = 1, 2, 3) \quad (5)$$

where $c_i = c_i(y)$ and $(D_i, k_3) = \text{constant}$. The axial component of the fluid velocity can be calculated using the analytical solution obtained by Cochran [5]. Indices $i = 1, 2, 3$ refer to oxygen in Reaction 1, Cu(I) complexes in Reaction 2 and Cu(II) complexes in Reaction 3, respectively. Stoichiometric coefficients μ_i are: $\mu_1 = -\frac{1}{4}$, $\mu_2 = -1$ and $\mu_3 = 1$.

Assuming, further, that the Reactions 1 and 2 are also first order and irreversible for oxygen and Cu(II) complexes, the boundary conditions at the disc surface, for $y = 0$, are expressed:

$$D_1 \frac{dc_1}{dy} \Big|_0 = k_1 c_{1,0} \quad (6)$$

$$D_2 \frac{dc_2}{dy} \Big|_0 = -2k_2 c_{3,0} \quad (7)$$

$$D_3 \frac{dc_3}{dy} \Big|_0 = -2D_1 \frac{dc_1}{dy} \Big|_0 + k_2 c_{3,0} \quad (8)$$

In the bulk of solution the asymptotic boundary conditions, for $y \rightarrow \infty$, are expressed:

$$c_1 = c_1^0 \quad (9)$$

$$c_2 = 0 \quad (10)$$

$$c_3 = c_3^0 \quad (11)$$

Introducing dimensionless variables, the boundary value problem (Equations 5–11) can be rewritten as mass transfer equations in the form:

$$\frac{d^2 C_i}{d\xi^2} - Sc_i H(\xi) \frac{dC_i}{d\xi} + \mu_i BS c_i C_1 C_2 = 0,$$

$$C_i = C_i(\xi), \quad (i = 1, 2, 3) \quad (12)$$

where, according to the Cochran solution [5],

$$H(\xi) = -0.51 \xi^2 + 0.333 \xi^3 - 0.103 \xi^4 + \dots$$

with boundary conditions for $\xi = 0$:

$$\frac{dC_1}{d\xi} \Big|_0 = W_1 C_{1,0} \quad (13)$$

$$\frac{dC_2}{d\xi} \Big|_0 = W_2 C_{2,0} \quad (14)$$

$$K_{3,2} \frac{dC_3}{d\xi} \Big|_0 = 2K_{1,2} \frac{dC_1}{d\xi} \Big|_0 - W_2 C_{2,0} \quad (15)$$

and for $\xi \rightarrow \infty$:

$$C_1^0 = 1 \quad (16)$$

$$C_2^0 = 0 \quad (17)$$

$$C_3^0 = c_3^0 / c_1^0 \quad (18)$$

The flux of copper entering the solution from the disc surface, $\xi = 0$, is the sum of the fluxes of Cu(I) and Cu(II) complexes and, in the presence of very fast Reaction 3 can be expressed by:

$$j_{\text{Cu}} = j_{\text{Cu(II)}} = - \left(D_2 \frac{dc_2}{dy} \Big|_0 + D_3 \frac{dc_3}{dy} \Big|_0 \right) \quad (19)$$

or in a dimensionless form, for $\xi = 0$:

$$j_{\text{Cu(II)}} = - \left(D_2 \frac{dC_2}{d\xi} \Big|_0 + D_3 \frac{dC_3}{d\xi} \Big|_0 \right) (\omega/\mu)^{1/2} C_1^0 \quad (20)$$

The solution of the boundary value problem formulated above allows calculation of the values of $j_{\text{Cu(II)}}$. To verify the model these values are compared with the fluxes of Cu(II) calculated from experimental data using the mass balance equation for Cu(II) complexes in the bulk solution which takes the form

$$j_{\text{Cu(II)}} = \frac{V}{A} \frac{dc_3^0}{dt} \quad (21)$$

The data from Zembura and Maraszewska's experimental study [1], given in the form of $n_{\text{Cu(II)}} = f(t)$, have been used in the calculations, with the initial condition $c_3^0(t = 0) = 0$.

3. Solution procedure

The non-linear form of the convective diffusion Equations 5 means that an analytical solution of the boundary value problem (Equations 12–18) cannot be obtained and a numerical method must be applied. The simple geometry of the system and the unidimensional form of the model allow the finite difference method to be employed. To improve the accuracy of calculated results a finite difference formulation with variable mesh spacing has been used [6].

Taking into consideration that the most significant changes of concentration occur in the vicinity of the disc surface the lengths of space increments, $\Delta\xi$ increased towards the bulk of solution. To ensure numerical stability of the finite difference scheme the forward analog for the first derivative and second-order correct for the second derivative have been used. The system of nonlinear algebraic equations has been solved by the modified Newton method. The value of the dimensionless coordinate ϕ_M was chosen in such a way that the condition

$$\left| \frac{C_{i,M-1} - C_{i,M}}{\Delta\xi_{M-1}} \right| < 10^{-4} \quad (22)$$

has to be satisfied in order to ensure the desired accuracy of numerical solution. Condition 22 was continuously examined during calculations and, when not satisfied, the solution domain was enlarged.

On the basis of the discrete distributions of Cu(I) and Cu(II) concentrations the molar flux of copper from the disc surface to the bulk solution was calculated according to Equation 20, in which the first derivatives were again approximated by forward finite difference analogs. Then utilizing an explicit scheme for Equation 21, the time concentration changes of c_3^0 were calculated from the equation

$$c_{3,t+\Delta t}^0 = c_{3,t}^0 + (A/V) j_{\text{Cu(I)}} \Delta t \quad (23)$$

with initial condition $c_3^0(t=0) = 0$.

The boundary value problem (Equations 12–18) was solved for different time levels.

4. Data for calculations

To solve the problem we assumed that the diffusion coefficient of dissolved oxygen in 1.0 M ammonia solution does not differ significantly from its value in 0.1 M H_2SO_4 being $D_1 = 1.74 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [7]. The oxygen solubility in ammonia solution was evaluated in the same manner for 0.1 M H_2SO_4 being equal to $c_1 = 1.15 \times 10^{-6} \text{ mol cm}^{-3}$ [8].

According to the data reported by Verkroost and co-workers [9] the polarographical diffusion coefficient for Cu(I) complexes was measured to be $D_2 = 1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Data can also be found in the literature [2, 9, 10, 11] to select diffusion coefficients for ammonia Cu(II) complexes; the most probable value is $D_3 = (10 \pm 0.2) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. For our calculation the value $D_3 = 1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was chosen. The kinematic viscosity of 1.0 M

ammonia solution was assumed to be equal to that of water, that is $\nu = 8.5 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$. Thus, the following Schmidt numbers and diffusivity ratio values were calculated, $Sc_1 = \nu/D_1 = 488.5$, $Sc_2 = \nu/D_2 = 566.7$, $Sc_3 = \nu/D_3 = 850.0$ and $K_{3,2} = D_3/D_2 = 0.667$, $K_{1,2} = D_1/D_2 = 1.16$. The surface area of the disc was 4.15 cm^2 and the volume of ammonia solution $V = 500 \text{ cm}^3$.

5. Discussion of calculation results

Based on the numerical solution, the value of oxygen limiting flux $j_{\text{O}_2} = \frac{1}{2} j_{\text{Cu(II)}}$ in the oxygen-saturated ammonia solution under 0.1 MPa pressure for a disc rotation speed of 25 r.p.s was calculated, (assuming $k_1 = 100$, $k_2 = k_3 = 0$ and $\omega = 2\pi f$) and its value was $1.22 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$. This was less than the value obtained from Levich's analytical formula [3]

$$j_{\text{O}_2} = 0.62 D_{\text{O}_2}^{2/3} \nu^{-1/6} \omega^{1/2} c_{\text{O}_2}^0 \quad (24)$$

which gives $1.35 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$.

The difference can be explained* if the simplifications of the Levich model are considered. To examine the influence of the length of the space increments, $\Delta\xi$, on the calculated results of the oxygen limiting flux, two different mesh spacings were used with $h_1 = 10^{-2}$, $M_1 = 21$ and $h_2 = 10^{-3}$, $M_2 = 50$, for which the oxygen limiting flux values were $1.22 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ and $1.24 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ respectively. Because this difference is less than the measurement error, the values of h_1 and M_1 were used in further calculations.

Based on the fact that Reaction 1, for copper dissolution with oxygen depolarization is controlled by diffusion [1] of oxygen, an infinite value for k_1 was assumed while k_3 for Reaction 3 (homogeneous oxidation of Cu(I) complexes) were treated as selectable arbitrarily chosen variables. Their most probable values were estimated as follows. Data for calculated and measured results [1] were introduced into the computer memory as input data with corresponding time values as output data. Values of $n_{\text{Cu(II)}}$ were then calculated according to the numerical algorithm for different reaction rate constants, k_2 and k_3 , and a sum of squares of differences between the measured and calculated values of $n_{\text{Cu(II)}}$ was determined. The results are shown in Table 1 and, according to the least squares principle, the values of $k_2 = 10^{-2} \text{ cm s}^{-1}$ and $k_3 = 0.5 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ can be chosen as the most probable. In the experimental work Sędzimir and co-workers [2] obtained the value $k_2 = 2.7 \times 10^{-2} \text{ cm s}^{-1}$ for similar ammonia solutions.

Figure 1 demonstrates measured results (marked by points) and calculated results (continuous lines) for different reaction rate constant values, k_2 . Circles, squares and triangles present three measurement series and it can be seen that reproducibility is not

* The value of oxygen limiting flux experimentally measured [12] by four-electron cathodic reduction of oxygen dissolved in 0.1 M oxygen-saturated ammonia solution under 0.1 MPa pressure for 25 r.p.s was $j_{\text{O}_2} = (1.5 \pm 0.2) \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$.

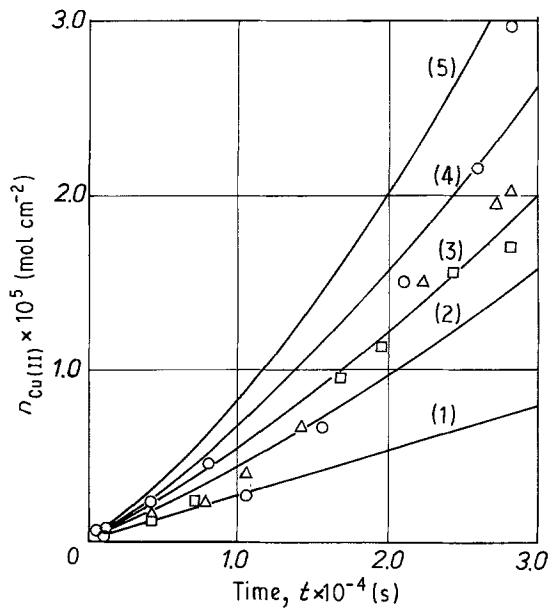


Fig. 1. Comparison of three series of experimental results (represented by O, □, Δ) and calculated results (continuous lines) of dissolution of the rotating copper disc in oxygen-saturated 1.0 M ammonia solution, oxygen pressure 0.1 MPa, temperature $25 \pm 0.2^\circ\text{C}$, 25 disc r.p.s. $k_1 = 100$. Curve (1): $k_2 = 0$, k_3 - arbitrary. curves (2), (3), (4) and (5): $k_2 = 5 \times 10^{-3}$; 10^{-2} , 3×10^{-2} , 10^2 cm s^{-1} , respectively, $k_3 = 0.5 \times 10^6 \text{ cm mol}^{-1} \text{ s}^{-1}$.

good. However, for reaction rate constants $k_1 = 10^2 \text{ cm s}^{-1}$ (asymptotic value), $k_2 = 10^{-2} \text{ cm s}^{-1}$ and $k_3 = 0.5 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ curve (3) seems to fit the measured data best. As mentioned earlier, the rate of the autocatalytic process is controlled by the rate of Reaction 2, which means that the reaction rate constant value, k_2 , is most important. This conclusion results directly from Fig. 2, in which the relationship between the sum of fluxes $j_{\text{Cu(II)}}$ from Reaction 1 and $j_{\text{Cu(I)}}$ from Reaction 2 is presented. It can also be seen that for $k_2 = 0$ we have $j_{\text{Cu(II)}} = 2j_{\text{O}_2}$ while $j_{\text{Cu(I)}} = 0$ and for $k_2 = 0.1$, $j_{\text{Cu(I)}} = 4j_{\text{O}_2}$ while $j_{\text{Cu(II)}} = 0$. Measurements of copper dissolution carried out at short times, to about 1000 s, shows that the flux $j_{\text{Cu(II)}} = 2j_{\text{O}_2}$ or slightly greater. This means that for time $t = 0$ we neglected the influence of Reaction 3 on the rate of the overall process.

Calculated results of dimensionless concentrations of C_1 , C_2 and C_3 against dimensionless coordinate ξ are presented in Fig. 3, from which the thickness of the diffusion layer can be evaluated; its value is as high as 10^{-3} cm for all species i .

Table 1. Sum of squares of differences between the measured and calculated values of $n_{\text{Cu(II)}}$.

$k_2 \times 10^3 \text{ (cm s}^{-1}\text{)}$	$k_3 \times 10^{-6} \text{ (cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\text{)}$				
	0.5	1.5	4.5	13.5	40.5
5.0	9.36	10.03	11.7	14.7	18.8
10.0	1.12	1.40	2.19	3.97	6.76
30.0	8.81	7.71	5.64	3.12	1.34
50.0	18.40	16.70	13.50	9.35	5.85

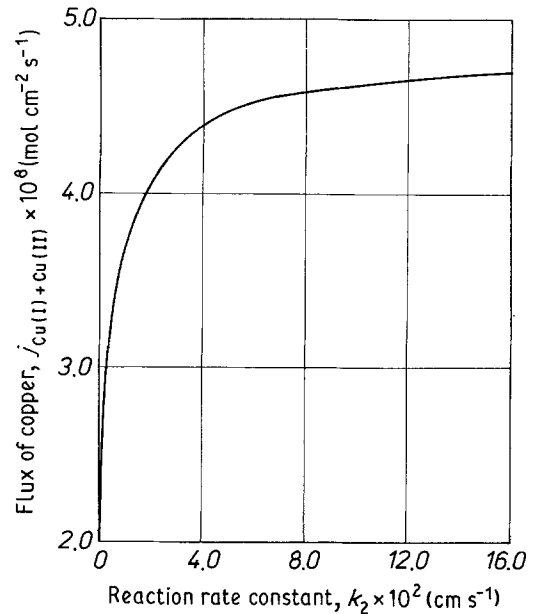


Fig. 2. Dissolved copper flux, j_{Cu} , against reaction rate constant, $k_2 \text{ cm s}^{-1}$ for $k_1 = 100 \text{ cm s}^{-1}$, $k_3 = 0.5 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $t = 0$, $B = 3.66 \times 10^{-3}$.

6. Conclusions

Comparison of the calculated results, based on the mathematical model proposed in this study, with measurements carried out by Zembura and Maraszewska [1] shows that the process of autocatalytic copper dissolution in oxygen-containing ammonia solutions proceeds according to the equations:

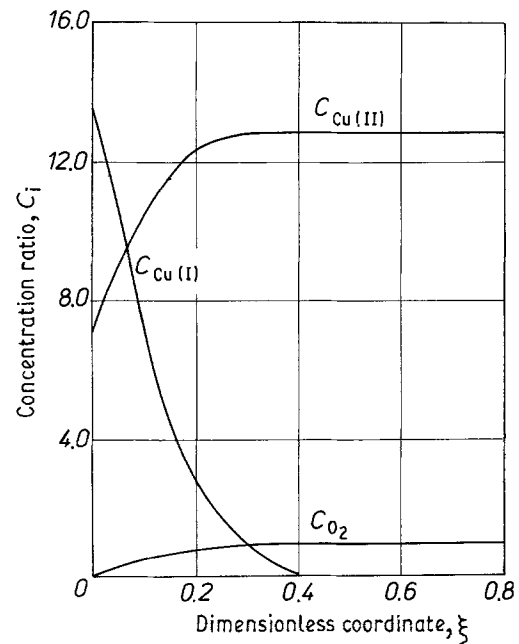


Fig. 3. Results of calculations of concentration ratio distribution: C_1 -oxygen, C_2 -Cu(I) complexes, C_3 -Cu(II) complexes for $t = 2.97 \times 10^3 \text{ s}$. $k_1 = 100 \text{ cm s}^{-1}$, $k_2 = 10^{-2} \text{ cm s}^{-1}$, $k_3 = 0.5 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $W_1 = 4.23 \times 10^4$, $W_2 = 4.905$ and $B = 3.66 \times 10^{-3}$.

where, in our case, $A_{(s)}$ is metallic copper and B, D, E are dissolved oxygen, cuprous and cupric ammonia complexes, respectively.

As mentioned earlier, substrate E, in the heterogeneous Reaction 26, is continuously reproduced in a rapid homogeneous reaction (27), making the overall process autocatalytic. Reaction 25 proceeds at a constant rate but its influence on the accumulation rate of product E in the bulk solution decreases with time. Based on the numerical evaluation of the reaction rate constants k_1 , k_2 and k_3 we can state that the rate of Reaction 26 controls the rate of the process of autocatalytic copper dissolution. Limited reproducibility of experimental results means that the reaction rate constant value, k_2 , can only be evaluated as $10^{-2} \text{ cm s}^{-1}$. Further analysis shows (see Fig. 2) that if the value of k_2 were one order of magnitude greater. Reaction 25 could not be identified in Zembura's and Maraszewska's experiments [1] and the scheme of the process would then be



and $j_{\text{Cu(I)}}$ should be equal to $4j_{\text{O}_2}$, while in the case of the model represented by Equations 25–27, $j_{\text{Cu(I)}} = 2j_{\text{O}_2}$

which is experimentally observed for short dissolution times [1].

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