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MECHANISM OF THE DISSOLUTION PROCESS OF COPPER IN ACIDIC COPPER SULPHATE SOLUTION AT EQUILIBRIUM POTENTIAL

By

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Abstract

The concentration C_s of Cu(I) ions in the vicinity of the Cu electrode was estimated in a thin layer cell at low current densities by measuring oxidation current densities on a detector electrode located at various distances from the working electrode. At the equilibrium potential of the processes $\text{Cu} \xrightleftharpoons{i_{1,0}} \text{Cu(I)} \xrightleftharpoons{i_{2,0}} \text{Cu(II)}$, a steady flow of Cu(I) ions from the Cu electrode surface to the detector electrode was established. The ratio of exchange current density of the elementary reactions was evaluated from the current observed on the detector electrode. This was found to be $i_{1,0}/i_{2,0} = (k_1/k_2) a_{\text{Cu(II),eq}}^{-1/2} = 6.0 \times 10^{-3} a_{\text{Cu(II),eq}}^{-1/2}$. This shows that the rate controlling step in the dissolution of copper is the step of production of Cu(I) from Cu, which is contradictory to that of other authors.

Introduction

MATTSSON and BOCKRIS¹⁾ proposed a mechanism for the deposition and dissolution reaction at the Cu/aq. CuSO₄, H₂SO₄ interface. They maintained that at low current densities, the rate controlling step is a reaction other than the charge transfer, analogous to the interpretation given to Ag electrode^{2,3)}. CONWAY and BOCKRIS⁴⁾, BOCKRIS and ENYO⁵⁾, BOCKRIS and KITA⁶⁾, and KITA, ENYO and BOCKRIS⁷⁾ emphasized that the copper electrode reaction at low current densities proceeds with a rate controlling surface diffusion of adions. BROWN and THIRKS⁸⁾ showed that at freshly electrocrystallized surfaces the lattice incorporation and dissolution steps are much faster than the cupric Cu(II)/cuprous Cu(I) step in the redox system over a wide potential range, except at small cathodic overpotential (<10 mV).

In this report, the authors present a new method for determining the

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activity ratio of $a_{\text{Cu(I)}}/a_{\text{Cu(II)}}^{1/2}$ at freshly electrocrystallized copper surface by a thin layer cell⁹⁾ at very low current densities, under the condition that the Cu/aq. CuSO₄, H₂SO₄ system is practically in equilibrium. Then the following reactions should be practically in equilibrium:



where Cu(0) is copper metal on the electrode and Cu(I) and Cu(II) are cuprous and cupric ions, respectively. The corresponding NERNST type equations are

$$E_{\text{I/0}} = E_{\text{I/0}}^0 - \frac{RT}{F} \ln(a_{\text{Cu(0)}}/a_{\text{Cu(I)}}), \quad (4)$$

$$E_{\text{II/I}} = E_{\text{II/I}}^0 - \frac{RT}{F} \ln(a_{\text{Cu(I)}}/a_{\text{Cu(II)}}), \quad (5)$$

$$E_{\text{II/0}} = E_{\text{II/0}}^0 - \frac{RT}{2F} \ln(a_{\text{Cu(0)}}/a_{\text{Cu(II)}}), \quad (6)$$

where a_i 's are activities and $a_{\text{Cu(0)}}$ taken to be unity. In equilibrium, the relations

$$E_{\text{I/0}} = E_{\text{II/I}} = E_{\text{II/0}} \quad (7)$$

are established, and hence they give

$$a_{\text{Cu(I),eq}}/a_{\text{Cu(II),eq}}^{1/2} = \exp\{(E_{\text{II/0}}^0 - E_{\text{I/0}}^0)F/RT\} = K, \quad (8)$$

where K is the equilibrium constant of the reaction $\frac{1}{2}[\text{Cu(0)} + \text{Cu(II)}] = \text{Cu(I)}$. Eq. (8) shows that at equilibrium, $a_{\text{Cu(I),eq}}$ at the electrode surface must have a definite value, when $a_{\text{Cu(II),eq}}$ has a given value. Suppose that we have a detector electrode near the Cu electrode, which captures Cu(I) ions produced at the copper electrode, and that their diffusion is rate controlling. Due to the concentration gradient Cu(I) ions diffuse towards the detector electrode according to FICK's first law, *i. e.*

$$J = D_{\text{Cu(I)}}(C_s - C_l)/l, \quad (9)$$

where J is the number of moles of Cu(I) ions transferred per unit time per unit area of the plane parallel to the working electrode W , and C_s and C_l are the concentrations of Cu(I) ions at the Cu electrode surface and at the detector electrode located at distance l , respectively. Suppose that

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detector electrode D oxidizes Cu(I) ions to Cu(II) ions completely. Then we may observe a steady current density i_D^s through the detector electrode, whose magnitude is given by, with $C_l=0$,

$$i_D^s = FD_{\text{Cu(I)}} C_s / l. \quad (10)$$

During the Cu(I) diffusion to the bulk according to Eq. (9), the reaction expressed by Eq. (1) and (2) must occur in such a way as to maintain the surface concentration C_s at a constant value with respect to $a_{\text{Cu(I)}}$ in Eq. (8). At the working electrode kept at the equilibrium potential, a current of density i_w , composed of net current of density i_1 and i_2 due to the reaction expressed by Eq. (1) and (2), may be observed,

$$i_w = i_1 + i_2, \quad (11)$$

where i_2 (reducing current) flows counterwise to i_1 . In the steady state, the rate of consumption of Cu(I) on the detector electrode equals that of production on the working electrode. Hence we have i_D^s , due to diffusion of Cu(I) ions, as

$$i_D^s = i_1 - i_2. \quad (12)$$

From Eq. (11) and (12), we have

$$i_1 = (i_w + i_D^s) / 2, \quad (13)$$

$$i_2 = (i_w - i_D^s) / 2. \quad (14)$$

Rewriting i_1 and i_2 by kinetic expressions proposed by VETTER, HURD or DELAHAY¹⁰, we have

$$i_1 = i_{1,0} \left[\exp \left\{ (1-\beta) F\eta / RT \right\} - (a_{\text{Cu(I)}} / a_{\text{Cu(I),eq}}) \exp (-\beta F\eta / RT) \right], \quad (15)$$

$$i_2 = i_{2,0} \left[(a_{\text{Cu(I)}} / a_{\text{Cu(I),eq}}) \exp \left\{ (1-\beta) F\eta / RT \right\} - \exp (-\beta F\eta / RT) \right], \quad (16)$$

$$i_{1,0} = k_1 a_{\text{Cu(I),eq}}^{-\beta}, \quad (17)$$

$$i_{2,0} = k_2 a_{\text{Cu(II),eq}}^{-\beta} a_{\text{Cu(I),eq}}^{\beta}, \quad (18)$$

where $i_{1,0}$ and $i_{2,0}$ are exchange currents and k_1 and k_2 are the specific rate constants of reaction (1) and (2), respectively, and η is the potential shift of electrode W from the equilibrium potential. Further, $a_{\text{Cu(I),eq}}$ and $a_{\text{Cu(II),eq}}$ are the activities of Cu(I) and Cu(II) ions at the surface of electrode W when electrode D is at $l=\infty$; and $a_{\text{Cu(I)}}$ is that at the surface of electrode W when electrode D is at $l=l$. The symmetry factor β may

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be assumed to be 1/2. Under the condition that the potential shift η is controlled to be sufficiently small, we have

$$\frac{i_w + i_D^s}{i_D^s - i_w} = \frac{i_1}{-i_2} = \frac{i_{1,0} \{1 - (a_{\text{Cu(I)}}/a_{\text{Cu(I),eq}})\}}{i_{2,0} \{1 - (a_{\text{Cu(I)}}/a_{\text{Cu(I),eq}})\}} = \frac{i_{1,0}}{i_{2,0}} = \frac{k_1}{k_2} a_{\text{Cu(II),eq}}^{-1/2} \quad (19)$$

Thus from the observed values of i_w and i_D^s and $a_{\text{Cu(II),eq}}$, we can determine the value of the ratio of $i_{1,0}$ to $i_{2,0}$ or of k_1 to k_2 .

Experimental

Reagents and solutions

All chemicals were of reagent grade and used without any further purification. Water used was distilled four times from a quartz still. Before every measurement, purified N_2 was bubbled into the solution for an hour to purge dissolved oxygen. All measurements were carried out at $21 \pm 1^\circ\text{C}$, in the presence of 0.05M H_2SO_4 and 0.05M Na_2SO_4 as supporting electrolytes.

Apparatus

In Fig. 1 are shown diagrams of the electric circuit and the thin layer cell. Potentials of electrode W and electrode D were controlled independently by two potentiostats. The constancy of the potentiostat was tested by a circuit composed of manganin resistors and condensers; it was proved that the fluctuation of the output potential of the potentiostat could be controlled within $\pm 3 \mu\text{V}$ during a time interval of 10 minutes or more. In actual practice once the potential is applied on the electrode W , the current i_w remains constant for more than 10 minutes, and the reliability of the magnitude of i_w remains within 1/10 of one division of the recorder chart, giving almost a straight line. Although the values of $i_w + i_D^s$ are of the order of $1 \mu\text{A}$, as is shown in Table 3, we can improve this effective value of $i_w + i_D^s$ so as to be around two, by setting the distance smaller. Electrode W and reference electrode R were of copper, deposited *in situ* on platinum plates from the same solution, whereas electrode D and common counter electrode C were of platinum.

The potential of electrode D was maintained so anodic that the surface concentration of Cu(I) ions on electrode D could be neglected. The distance between electrode W and D was controlled by moving electrode D , fixed on a moving spindle of a micrometer, relative to electrode W , mounted on the fixed axis of the micrometer.

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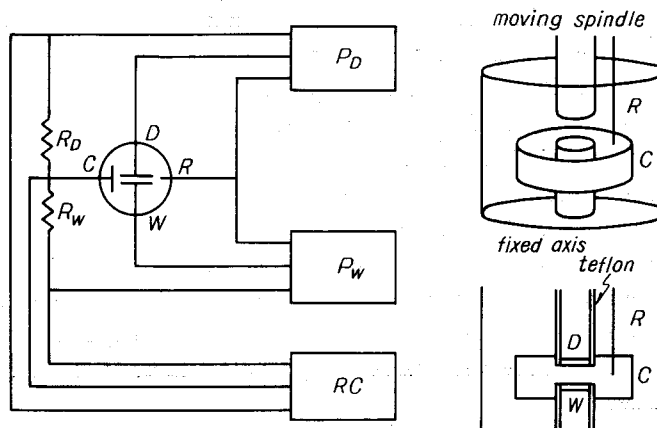


Fig. 1. Diagram of the electric circuit and the thin layer cell.

C : common counter electrode P_D, P_W : potentiostat
 D : detector electrode RC : recorder
 W : working electrode R_D, R_W : resistance
 R : reference electrode

Results

Verification of the presence of Cu(I) ions at the Cu/CuSO₄, H₂SO₄ interface at equilibrium potential

When the working electrode W was maintained at equilibrium potential, an oxidizing current i_D on the detector electrode D was appreciable only

TABLE 1. Summary of the experiments to determine the conditions under which Cu(I) ions can be detected.

Solutions: 0.05M H₂SO₄+0.05M Na₂SO₄+xM CuSO₄, 21±1°C. OP: open circuit potential, EQ: equilibrium potential, UN: under potential, potential region where cathodic current flows through the Pt-electrode, but it exists at a potential more positive than EQ: cf. ref. (12).

Conditions		Run							
		1	2	3	4	5	6	7	8
Electrode	Material	Pt	Pt	Cu	Cu	Cu	Pt	Pt	Cu
	Potential	OP	OP	OP	OP	EQ	UN	UN	EQ
CuSO ₄	(M)	0.5	0.5	none	none	0.5	0.5	0.5	0.5
Distance	(mm)	2.00	0.05	2.00	0.05	2.00	2.00	0.05	0.05
i_D^s	(μ A)	—undetectable—						20	20

in case 8 (Table 1): this means that i_D originates only from the oxidation of Cu(I) ions present and not from impurities in the solution. In case 7, the presence of Cu(I) ions, produced by cathodic reduction of Cu(II) ions on the Pt working electrode, could be detected only in the space close to the electrode surface. The Cu(I) ions, thus produced, must migrate into the bulk of the solution and, in a stationary state, give a steady current density i_D^s obeying FICK's first law, Eq. (10). Experimental results presented in Fig. 2 satisfy Eq. (10), *i.e.* the relation i_D^s vs. $1/l$.

The efficiency of collecting Cu(I) ions, produced at electrode *W* by electrode *D*, was determined to be 0.99 ± 0.004 by experiments described elsewhere*). Thus, observed values $i_{D,obs}^s$ were divided by 0.99 to obtain correct i_D^s values.

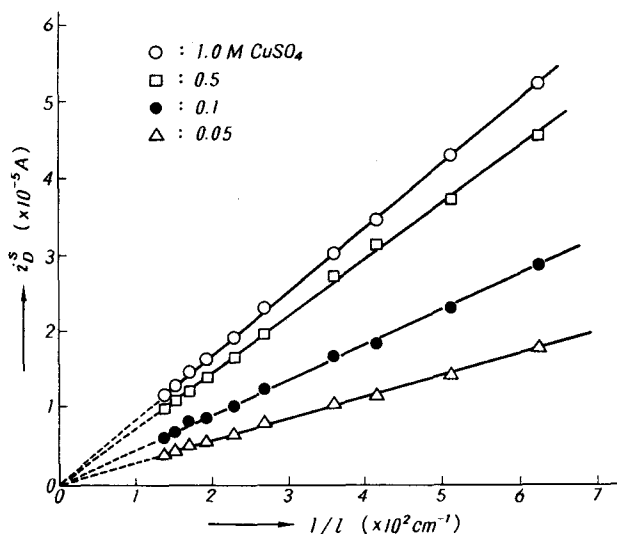


Fig. 2. i_D^s vs. $1/l$ for several concentrations of Cu(II).

Determination of the diffusion coefficient $D_{Cu(I)}$ and the surface concentration C_s of Cu(I) ions in Eq. (10)

In the steady state of the diffusion process of Cu(I) ions, the concentration gradient $(C_s - C_l)/l$ should be linear so that the total electricity Q , charged on Cu(I) ions in the layer between the two parallel electrodes *W* and *D*, is expressed as

$$Q = nFA \int_0^l -C_x dx = nFA \int_0^l -\frac{C_s}{l} x dx = nFA l C_s / 2, \quad (20)$$

*) Hajime CHIBA: Bachelor's Thesis (in Japanese).

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where A is the surface area of the electrode. This is also given by

$$Q = \int_0^{\infty} i_D^* dt, \quad (21)$$

where i_D^* is the current which flows after electrode W has ceased production of Cu(I) ions, as illustrated in Fig. 3. From Eqs. (10) and (20) we have

$$D_{\text{Cu(I)}} = i_D^{*2} / 2Q. \quad (22)$$

The value of $D_{\text{Cu(I)}}$ thus obtained was 3.4×10^{-6} (cm²/sec), and was comparable to the values of other ions in the literature.

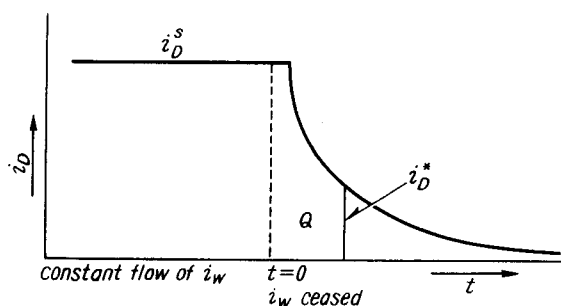


Fig. 3. Illustration of the determination of the Q value.

The ratio $a_{\text{Cu(I)}}/C_s$ gives activity coefficient γ , which depends upon C_s and the ionic strength I of the solution. However, in a set of preliminary experiments in which the concentration of Cu(II) ions was kept at a constant value while the I -values were changed (0.5–3.2), the authors obtained the same value of C_s according to Eq. (10). In view of this result, that is, that changes of the ionic strength did not alter the value of C_s at the electrode surface, and also since the value of C_s was very low, the authors

TABLE 2. Equilibrium activities of Cu(I) ions and Cu(II) ions for various concentrations of CuSO₄

Solution: 0.05M H₂SO₄ + 0.05M Na₂SO₄ + x M CuSO₄,
21°C. I -value: 0.5–4.3

Concentration of CuSO ₄ (M)	$a_{\text{Cu(II)}}$ ($\times 10^{-2}$)	$a_{\text{Cu(I)}}$ ($\times 10^{-6}$)	K ($\times 10^{-6}$)
1.0	6.5	0.75	3.0
0.5	4.5	0.66	3.1
0.1	1.6	0.41	3.2
0.05	0.7	0.26	3.1

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assumed thereby that $\gamma = \text{constant} \leq 1$, although in the main experiments the range of the ionic strength was somewhat larger than in the preliminary experiments. Moreover, if $\gamma = 1$ is assumed, we obtain the upper limit of $a_{\text{Cu(II),eq}}$ and of K in Eq. (8); and the results of the main experiments are shown in Table 2. These clearly indicate that the relationship of Eq. (8) is a consequence of the equilibrium which exists at the interface. The values of $a_{\text{Cu(II)}}$ were obtained from other experiments in accordance with Eq. (6).

Ratio of k_1 to k_2 in Eq. (19)

Table 3 shows the results obtained at several concentrations of CuSO_4 . The value of the ratio k_1 to k_2 is 6.0×10^{-3} in every case. This means that in the electrode process of copper in acidic copper sulphate solution at equilibrium potential, the rate controlling process is that defined by Eq. (1).

TABLE 3. Ratio of the exchange current $i_{1,0}$ to $i_{2,0}$ and of the specific rate constant k_1 to k_2 .

Solution: 0.05M $\text{H}_2\text{SO}_4 + 0.05\text{M Na}_2\text{SO}_4 + x\text{M CuSO}_4$,
21°C. I -value: 0.5–4.3

CuSO_4 (M)	$-i_w$ (μA)	i_D^S (μA)	$\frac{i_{1,0}}{i_{2,0}}$	$a_{\text{Cu(II)}}^2$ ($\times 10^{-1}$)	k_1/k_2 ($\times 10^{-3}$)
1.0	26.5	27.8	0.024	2.5	6.0
0.5	15.2	16.1	0.029	2.1	6.1
0.1	9.4	10.3	0.045	1.3	5.9
0.05	5.5	6.4	0.071	0.84	6.0

Discussion

The experimental results are in good accord with those theoretically derived and lead to the conclusion that under the given condition the rate controlling step is that of production of cuprous ion from copper. BOCKRIS and others reported that at high polarization regions the rate controlling step is the reduction of cupric to cuprous ion. KITA, ENYO and BOCKRIS discussed the possibility of change in the surface density of screw dislocations as active points, with change in electrode potential, on the basis of the slow surface diffusion mechanism, which is considered kinetically important at low current densities. A similar view that high current densities can activate silver electrode was also presented by DESPIC and BOCKRIS⁽¹⁾. The present authors agree with both of these reports insofar as is concerned the change in the surface density of the active points on the electrode

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surface as a function of the electrode potential; but regarding the function of the active points, we take the different view that they are active only in the reduction of cuprous ion to copper and *vice versa*, and do not affect the cupric-cuprous reaction in any way. The latter reaction may occur evenly on the whole plane of the outer HELMHOLTZ layer, and ions produced diffuse freely to the bulk of the solution according to their concentration gradients. The activity of active points may differ from point to point, and moreover the activity of each point may differ according to the environmental circumstances.

These views have to be confirmed by other experimental results. The authors will report on some of them in the near future.

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