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## Investigation of Oxidation of Copper by Use of Radioactive Cu Tracer

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A very thin layer of radioactive copper was electrolytically deposited on a copper blank. The surface was then oxidized in air at 1000°C for 18 minutes, giving an oxide layer with a thickness of  $1.25 \times 10^{-2}$  cm. After quenching, successive layers of the oxide were removed chemically, and the copper activity in each layer was measured. The observed self-diffusion of radioactive copper in the oxide agrees quantitatively with a theory based on the following assumptions: (a) The oxide grows by diffusion of vacant  $\text{Cu}^+$  sites from the outer surface of the oxide inward to the metal. (b) The concentration of vacant sites at the oxygen-oxide interface is independent of the oxide thickness, and drops linearly from this constant value to zero at the metal boundary. (c) Accompanying the inward flow of vacant sites, there is a flow of positive electron holes such as to maintain electrical neutrality. (d) Self-diffusion of copper ions takes place only by motion into vacant sites. The results give a fairly direct confirmation of the theory of oxidation first suggested by Wagner.

## I. INTRODUCTION

FRENKEL, Schottky, Jost, and particularly Wagner,<sup>1</sup> have explained ionic conductivity and diffusion in solids as resulting from certain types of lattice defects (departures from perfect periodicity) which are in equilibrium with the lattice at high temperatures. Wagner<sup>2</sup> has extended these ideas to explain rates of reactions in the solid state which are limited by the diffusion of one of the constituents.

At high temperatures, copper oxidizes in the presence of oxygen gas in the form of a uniform film of  $\text{Cu}_2\text{O}$  which, except for very thin films, increases in thickness proportionally with the square root of the time. The rate of growth increases rapidly with increasing temperature, and also depends on the oxygen gas pressure.<sup>3</sup> On the basis of a large number of experiments,<sup>4</sup>

Wagner and co-workers have developed a theory to account for the reaction rate which includes the following assumptions:

(a) The lattice defects in  $\text{Cu}_2\text{O}$  are vacant sites ordinarily occupied by  $\text{Cu}^+$  ions (so-called Schottky defects). These vacant sites have an effective negative charge of one electron.

(b) Electrical neutrality is maintained by an equivalent number of positive electron holes (electrons missing from the uppermost filled band). These electron holes are responsible for the electrical conductivity of  $\text{Cu}_2\text{O}$ .

(c) The electron holes and vacant sites are completely dissociated at temperatures of the order of 1000°C. There may, however, be incomplete disorder of the Debye-Hückel type.

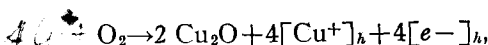
(d) The equilibrium number of vacant sites depends on the pressure of the oxygen gas in contact with the oxide. The concentration in equilibrium with metallic copper is small. During oxidation, there is a concentration gradient of vacant  $\text{Cu}^+$  sites extending from the oxygen interface to the metal.

(e) The oxide is formed at the oxygen interface. The  $\text{Cu}^+$  ions arrive by diffusion from the metal through the oxide.

(f) The mechanism of diffusion of the  $\text{Cu}^+$  ions is by motion of vacant sites from the oxygen interface to the metal.

(g) Electrical neutrality is maintained by an equal current of positive electron holes from the oxygen interface to the metal.

The equation for the reaction at the oxygen interface may be expressed in the form



in which  $[\ ]_h$  indicates a vacancy or defect  $\text{Cu}^+$  ion or electron. Correspondingly, at the metal

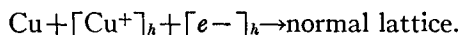
<sup>1</sup> See, for example, W. Jost, *Diffusion und Chemische Reaktion in festen Stoffen* (T. Steinkopff, Dresden, 1937), or N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1940), Chaps. II and VIII.

<sup>2</sup> C. Wagner, *Zeits. f. physik. Chemie* **B21**, 25 (1933); **B32**, 447 (1936); C. Wagner and K. Grönewald, *Zeits. f. physik. Chemie* **B40**, 455 (1938). See also C. Wagner, *Trans. Faraday Soc.* **34**, 851 (1938), N. F. Mott, *Trans. Faraday Soc.* **36**, 472 (1940).

<sup>3</sup> N. B. Pilling and R. E. Bedworth, *J. Inst. Metals* **29**, 529 (1923). A logarithmic law is followed at low temperatures. Cf. B. Lustman and R. F. Mehl, *Metals Tech.* **8**, 1317 (1941).

<sup>4</sup> The first comprehensive experiments are those of H. Dünwald and C. Wagner, *Zeits. f. physik. Chemie* **B22**, 212 (1933). Later experiments, together with a comparison of theoretical and experimental values for the rate of oxidation, are summarized by C. Wagner and K. Grönewald, reference 2.

interface



The vacant  $\text{Cu}^+$  sites are filled by  $\text{Cu}^+$  ions from the metal and the electron defects are filled by electrons from the metal thus eliminating the two holes and leaving the normal lattice in their place. Except when the oxide layer is very thin, the rate of reaction is limited by diffusion of the vacant sites from the oxygen interface to the metal. A very much simplified version of Wagner's theory is given in Section III.

It may be appropriate to make some brief remarks about the experimental basis for Wagner's assumptions. Wagner and co-workers<sup>4</sup> have measured the rate of oxidation, and also a number of properties of  $\text{Cu}_2\text{O}$  in equilibrium with  $\text{O}_2$ , at various pressures, with the following conclusions:

(a) The rate constant for oxidation varies with oxygen pressure as  $p^{1/7}$ .

(b) The electrical conductivity<sup>5</sup> is also proportional to  $p^{1/7}$ .

(c) The stoichiometric excess of O in  $\text{Cu}_2\text{O}$ , as determined chemically,<sup>6</sup> is proportional to  $p^{1/5}$ .

(d) The transport number<sup>7</sup> for ionic conduction in  $\text{Cu}_2\text{O}$  indicates that vacant  $\text{Cu}^+$  sites carry  $5 \times 10^{-4}$  of the current at  $1000^\circ\text{C}$ .

Elementary theory, assuming complete dissociation of electron defects, and vacant sites, predicts that the excess oxygen should vary as  $p^{1/8}$ . Complete association would give a  $p^{1/4}$  dependence. The observed  $p^{1/5}$  dependence is intermediate, suggesting partial dissociation. Another possibility, suggested by Wagner and Hammer,<sup>6</sup> is that dissociation is complete, but that there is incomplete disorder of the Debye-Hückel type. If it is assumed that dissociation is complete, so that there are two defect electrons for each excess O atom, the number of electrons as determined from the stoichiometric excess, together with the electrical conductivity, indicate a mobility of about  $1 \text{ cm}^2/\text{volt sec.}$  at  $1000^\circ\text{C}$ .<sup>8</sup> This value is only a little smaller than one would predict from extrapolations of mobilities deter-

mined from the Hall effect at lower temperatures. Thus a reasonable fraction of the centers must be dissociated.

As outlined in Section III, Wagner has shown that the rate of reaction can be determined from the equilibrium number of vacant sites, the electrical conductivity, and the transport number. Assuming complete dissociation, approximate agreement with directly measured values was obtained.<sup>4</sup> This agreement, together with the fact that the rate constant varies with pressure in the same way as the electrical conductivity, indicates that diffusion during oxidation is mainly by dissociated vacant sites. If there is an appreciable number of neutral associated centers, their mobility must be so small that they do not contribute appreciably to the reaction.

In order to investigate further the diffusion of copper ions during oxidation, we have performed an experiment using a radioactive copper tracer. A thin coating of radioactive copper was electroplated on a copper blank. The surface was oxidized in air at atmospheric pressure at a temperature of  $1000^\circ\text{C}$  for 18 minutes, giving an oxide film with a thickness of about  $0.0127 \text{ cm}$ . The distribution of radioactive copper in the film was then determined. We are here concerned with the self-diffusion of copper in  $\text{Cu}_2\text{O}$  which has a varying concentration of vacant sites.

There are two possible mechanisms for self-diffusion:

(a) Motion of copper ions into vacant sites. This mechanism will contribute a term to the diffusion coefficient proportional to the concentration of vacant sites.

(b) Interchange of two neighboring  $\text{Cu}^+$  ions in the lattice. The probability should be independent of the concentration of vacant sites.

Our results indicate that the mechanism of self-diffusion is (a) rather than (b). Good agreement between calculated and experimental results is obtained if the distribution of vacant sites is assumed to vary in position and time in accordance with Wagner's theory of the oxidation reaction. Our results thus confirm Wagner's theory, without reference to conductivity experiments.

## II. EXPERIMENTAL PROCEDURE AND RESULTS

The experimental work described in this paper was done in 1938, but publication was delayed

<sup>5</sup> J. Gundermann, K. Hauffe, and C. Wagner, *Zeits. f. physik Chem.* **B37**, 148 (1937).

<sup>6</sup> C. Wagner and H. Hammer, *Zeits. f. physik Chemie* **B40**, 197 (1938).

<sup>7</sup> J. Gundermann and C. Wagner, *Zeits. f. physik Chemie* **B37**, 155 (1937).

<sup>8</sup> There is apparently a numerical error of a factor of ten in the calculations of reference 6.

TABLE I. Determination of the thicknesses of oxide layers from change in weight during etching.

| Sample       | Weight in grams |       |       | Thickness in cm       |
|--------------|-----------------|-------|-------|-----------------------|
|              | before          | after | diff. |                       |
| 1            | 8.097           | 7.936 | .161  | $1.6 \times 10^{-3}$  |
| 2            | 7.936           | 7.469 | .467  | $4.67 \times 10^{-3}$ |
| 3            | 7.469           | 7.121 | .348  | $3.48 \times 10^{-3}$ |
| 4*           | 7.121           | 6.714 | .407  |                       |
| Oxide in 4** |                 |       | .300  | $3.00 \times 10^{-3}$ |
| Total oxide  |                 |       | 1.27  | $12.7 \times 10^{-3}$ |

\* This includes some of the underlying copper.

\*\* By difference.

because the results are rather incomplete. Because of the stress of other work and the intervention of the war, further experimental work has been postponed indefinitely so that it has been decided to publish the available data, together with a recent theoretical analysis of the problem, at this time.<sup>9</sup>

The copper blank used in the experiment was electroplated with radioactive copper by J. Steigman, then at Columbia University. The technique used is exactly the same as that used for the preparation of blanks for a study of the self-diffusion of copper in the metal, done about the same time.<sup>10</sup>

Sufficient radioactive copper (Cu 64, period of decay, 12.8 hours) was deposited on one side of a copper blank, to give an activity of about 2000 counts per minute. The blank was then oxidized in air at atmospheric pressure at 1000°C for 18 minutes, was kept at 500°C for 3 minutes, and then quenched in air. The oxide film was formed only on the active side of the blank. The back of the blank was protected by another sheet of copper. At 1000°C the oxide film formed is all Cu<sub>2</sub>O. At 500°C a thin film of black CuO is formed on the surface of the Cu<sub>2</sub>O. The total thickness of the oxide was determined by the increase in weight of the copper blank after oxidation (weight of O<sub>2</sub> absorbed). This thickness was  $12.7 \times 10^{-3}$  cm. The CuO layer was less than 10 percent of this.

Successive layers of oxide were removed by etching the oxidized face of the copper blank in

<sup>9</sup> The experimental work was done by the second and third named authors. The first named author has been concerned only with the theoretical interpretation and analysis of results.

<sup>10</sup> The method is described by J. Steigmann, W. Shockley, and F. C. Nix, Phys. Rev. **56**, 13 (1939). See also J. Steigmann, Phys. Rev. **53**, 771 (1938).

TABLE II. Percent of radioactive copper in successive layers as determined from tests of activity.

| Sample | Wt. of Cu tested mg | Counts in 5 min. | Counts per min. per mg corrected for background | Percent of total activity in sample |
|--------|---------------------|------------------|---|-------------------------------------|
| 1      | 21                  | 218              | 1.2   | $22.5 \pm 2$                        |
| 2      | 17                  | 180              | 1.0   | $55.0 \pm 6$                        |
| 3      | 27                  | 155              | 0.45  | $17.5 \pm 2.5$                      |
| 4      | 27                  | 108              | 0.11  | $5.0 \pm 2.5$                       |

nitric acid. After each etch the blank was washed in water, dried, and weighed. These weights and the calculated thickness of oxide in each sample are given in Table I. The nitric acid and the water used in washing the blank after each etch were saved. The copper from each successive etch was precipitated from the mixture of nitric acid and wash water as copper sulfide. Four successive layers were etched off. The last one included some of the underlying copper.

Some of the wet copper sulfide powder from each sample was tested for activity by spreading it out on filter paper, allowing it to dry, and wrapping it around the counter. The results of these tests are given in Table II. The total activity in each layer is determined by multiplying the activity per mg by the total weight of each sample (see Table I). The last column gives this activity in percent. The probable errors listed were determined from the number of counts. Other possible errors are smaller.

### III. WAGNER'S THEORY OF OXIDATION

Wagner's theory of oxidation, as applied to the formation of Cu<sub>2</sub>O, may be outlined briefly as follows.<sup>11</sup> Let  $x$  represent the distance of a point in the oxide from the metal surface. Let  $n_e(x)$  and  $n_i(x)$  represent the concentrations (number per cm<sup>3</sup>) of (dissociated) defect electrons and vacant sites, respectively. For an electrostatic field  $F(x)$  in the oxide, the electronic and ionic current densities, from both diffusion and conduction, are

$$I_e = -eD_e(\partial n_e / \partial x) + \sigma_e F(x) \quad (1)$$

and

$$I_i = eD_i(\partial n_i / \partial x) + \sigma_i F(x), \quad (2)$$

<sup>11</sup> The following is a much simplified version of Wagner's theory, and is presented to introduce equations needed for later reference. Cf. N. F. Mott, reference 2.

where  $D$  and  $\sigma$  represent diffusion coefficients and conductivities, respectively. For equal concentrations,  $D_e$  and  $\sigma_e$  differ from  $D_i$  and  $\sigma_i$  by the ratio of the electronic to the ionic mobilities, a large factor.<sup>12</sup>

Since the space charge is limited,  $n_e \simeq n_i$  throughout most of the layer. Each term on the right of Eq. (1) therefore differs from the corresponding term of Eq. (2) by the ratio of the mobilities. Furthermore, since there is no net current,  $I_e = -I_i$ , so that  $I_e$  must be small compared with either term on the right-hand side of Eq. (1). In other words,  $I_e$  represents a small difference between two nearly equal terms. The electrostatic field,  $F(x)$ , of course, adjusts in such a way that these conditions are satisfied. Since the two terms on the right-hand side of Eq. (2) differ from those of Eq. (1) by a constant factor, they must also be nearly equal. However, instead of subtracting, they add, so that we have approximately

$$I_i = 2eD_i(\partial n_i / \partial x). \quad (3)$$

Consequently the effect of the electrostatic field in the oxide is to double the current to be expected from diffusion alone. Equation (3) is a special case of a more general expression derived by Wagner, which was in turn based on a similar equation for the diffusion of electrolytes.

Except during the initial stages, the rate of oxidation is controlled by diffusion of Cu from the metal to the oxygen interface. Diffusion of a vacant  $\text{Cu}^+$  site from the oxygen interface to the metal is equivalent to the motion of one  $\text{Cu}^+$  ion from the metal to the outside surface. The copper ion current (ions per unit area per unit time) can be obtained from the current (3) by dividing by  $e$ , the charge per ion. This current must be divergenceless (except for a very small contribution used to readjust the value of  $n_i$  as the layer grows). Consequently,  $\partial n_i / \partial x$  is independent of  $x$  through the layer.

Let  $X(t)$  be the thickness of the oxide layer at time  $t$ , and suppose that in time  $dt$  the thickness increases by  $dX$ . Let  $N$  be the normal number of  $\text{Cu}^+$  ions per unit volume. The number of  $\text{Cu}^+$  ions which diffuse in time  $dt$  is then equal

to  $NdX$ , and making use of Eq. (3),

$$\frac{dX}{dt} = \frac{2D_i}{N} \frac{\partial n_i}{\partial x}. \quad (4)$$

It is assumed that the concentrations of vacant sites at the metal and oxygen interfaces are determined by local reactions and are independent of the thickness of the layer. Denoting their difference by  $\Delta n_i$  we have

$$\partial n_i / \partial x = \Delta n_i / X. \quad (5)$$

If Eq. (5) be substituted into Eq. (4), we find that the rate of growth is inversely proportional to the oxide thickness,

$$dX/dt = K/X, \quad (6)$$

where the rate constant  $K$  is

$$K = 2D_i \Delta n_i / N. \quad (7)$$

The thickness at time  $t$  as obtained from integration of (6) is

$$X = (2Kt)^{1/2} = 2(D_i \Delta n_i / N)^{1/2}. \quad (8)$$

The approximate validity of Eqs. (7) and (8) has been checked by Wagner and Grünwald.<sup>2</sup> The coefficient of diffusion was obtained from Einstein's relation,  $eD_i = v_i kT$ . The mobility  $v_i$  was derived from measurements of the transport number for ionic conduction,  $\tau_i$ , the electrical conductivity,  $\sigma$ , and the number of vacant sites,  $n_i$  (the latter from the stoichiometric excess of 0):

$$v_i = \sigma \tau_i / en_i.$$

Thus, in terms of measured quantities,

$$K = (2\sigma \tau_i kT / e^2 N) (\Delta n_i / n_i). \quad (7a)$$

This expression, which is slightly different from the one used by Wagner and Grünwald, gives good agreement with the observed rate of reaction. It should be noted that only the relative values of the concentration of vacant sites appears. An appreciable number of associated centers (defect electrons + vacant sites) could exist without affecting the agreement provided that

(a) The degree of dissociation does not vary greatly with concentration.

(b) The diffusion constant of associated centers is considerably less than that of dissociated vacant sites.

<sup>12</sup> About  $2 \times 10^3$  at  $1000^\circ\text{C}$  (reference 6).

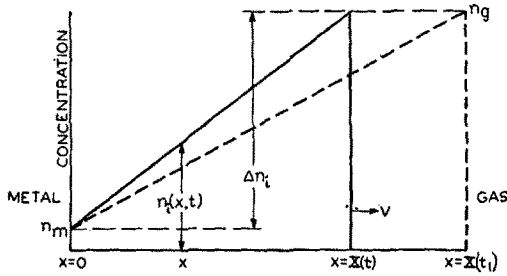


FIG. 1. Schematic diagram of oxide layer showing concentration  $N_i(x, t)$  of vacant  $\text{Cu}^+$  sites at successive times.

#### IV. THEORY OF DIFFUSION OF RADIOACTIVE Cu

One mechanism by which diffusion of radioactive Cu can take place is by motion into a vacant lattice site. The vacant site may move into any neighboring site, but a  $\text{Cu}^+$  ion will diffuse only if a neighboring  $\text{Cu}^+$  site is vacant. This mechanism will give a contribution to the self-diffusion coefficient for  $\text{Cu}^+$  ions equal to the diffusion coefficient for vacant sites,  $D_i$ , times the probability that a given neighboring site is vacant,  $n_i/N$ . This part of the self-diffusion coefficient may depend both on the position within the oxide layer and on the time:

$$D_i n_i(x, t)/N. \quad (9)$$

According to Eq. (5), the concentration of vacant sites varies linearly with  $x$ , increasing from a small value,  $n_m$ , at the metal interface to  $n_g = n_m + \Delta n_i$  at the oxygen interface. We may set

$$n_i(x, t) = n_m + x \Delta n_i / X. \quad (10)$$

We assume  $n_m$  and  $\Delta n_i$  are constant, and that the thickness of the layer,  $X$ , increases with time according to Eq. (8).

In addition to diffusion by motion into vacant sites, it is conceivable that two adjacent  $\text{Cu}^+$  ions may change places. This would give a constant contribution to the self-diffusion coefficient, indistinguishable from that resulting from a uniform distribution of vacant sites, as obtained, for example, from the constant term  $n_m$  in Eq. (10). Thus we assume for the self-diffusion coefficient,  $D$ , for  $\text{Cu}^+$  ions:

$$D = D_0 + D_i \frac{\Delta n_i}{N} \frac{x}{X}. \quad (11)$$

Replacing  $X$  by its value from Eq. (8),

$$D = D_0 + \frac{1}{2} (D_i \Delta n_i / N)^{1/2} (x/t)^{1/2}. \quad (12)$$

We are now ready to derive the self-diffusion equation appropriate during oxidation. Figure 1 shows the oxide layer at any time  $t$ . The concentration of vacant sites increases linearly from  $n_m$  at the metal interface ( $x=0$ ) to  $n_g$  at the oxygen interface ( $x=X$ ). The oxygen interface is moving to the right with a velocity

$$V = dX/dt = (D_i \Delta n_i / N t)^{1/2}. \quad (13)$$

The current of radioactive  $\text{Cu}^+$  ions at any point  $x$  in the layer will be the sum of two terms: a diffusion current,  $-D(\partial c / \partial x)$ , due to the concentration gradient, and a drift term,  $Vc$ , proportional to the concentration, which comes from the drift of  $\text{Cu}^+$  ions from the metal to the oxygen interface as the layer grows. Thus the total current is

$$-D(\partial c / \partial x) + Vc. \quad (14)$$

The rate of change of concentration with time is equal to the negative of the gradient of the current

$$\begin{aligned} \frac{\partial c}{\partial t} &= -\frac{\partial}{\partial x} \left( -D \frac{\partial c}{\partial x} + Vc \right) \\ &= D \frac{\partial^2 c}{\partial x^2} - \left( V - \frac{\partial D}{\partial x} \right) \frac{\partial c}{\partial x}. \end{aligned} \quad (15)$$

Comparison of (12) and (13) shows that

$$V = 2(\partial D / \partial x), \quad (16)$$

so the diffusion equation becomes

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \frac{\partial D}{\partial x} \frac{\partial c}{\partial x}, \quad (17)$$

with  $D$  given as a function of  $x$  and  $t$  by Eq. (11) or (12).

There is a quasi-stationary solution of Eq. (17) of the form

$$c = \frac{1}{t^{1/2}} g(x/X), \quad (18)$$

which keeps the same shape as the layer increases in thickness, with the concentration at similar points decreasing inversely with the square root of the time. Regardless of the initial conditions

existing when the layer is very thin, this solution will be approached as the layer increases in thickness. This is the solution of interest.

In order to simplify the resulting equations, we set

$$z = x/X, \quad (19)$$

$$D_1 = D_i \Delta n/N, \quad \alpha = D_0/D_i, \quad (21)$$

so that we have the following:

$$D = D_0 + D_1 Z = D_1(\alpha + z), \quad (22)$$

$$\frac{\partial c}{\partial t} = -\frac{1}{2t^{1/2}} g - \frac{1}{2t^{1/2}} \frac{dg}{dz}, \quad (23)$$

$$\frac{\partial D}{\partial x} \frac{\partial c}{\partial x} = \frac{1}{t^{1/2}} \frac{D_1}{X^2} \frac{dg}{dz} = \frac{1}{4t^{1/2}} \frac{dg}{dz}, \quad (24)$$

$$\frac{\partial^2 c}{\partial x^2} = \frac{1}{t^{1/2}} \frac{1}{X^2} \frac{d^2 g}{dz^2} = \frac{1}{4D_1 t^{1/2}} \frac{d^2 g}{dz^2}. \quad (25)$$

Substituting into Eq. (17) yields an ordinary differential equation,

$$(z + \alpha) \frac{d^2 g}{dz^2} + (2z - 1) \frac{dg}{dz} + 2g = 0. \quad (26)$$

This equation may be expressed in the form

$$\frac{d}{dz} \left( (z + \alpha) \frac{dg}{dz} + 2(z - 1)g \right) = 0. \quad (27)$$

The interpretation is that the gradient of the current in the relative coordinate system ( $z$  coordinates) is zero. This is the requirement for quasi-stationary solution.

Since the flow of radioactive  $\text{Cu}^+$  ions is zero at the oxygen interface ( $z = 1$ ), the current itself must vanish:

$$(z + \alpha) \frac{dg}{dz} + 2(z - 1)g = 0. \quad (28)$$

In terms of the  $x$  coordinate system, Eq. (28) implies that

$$\begin{aligned} -D(\partial c/\partial x) + Vc &= 0 \text{ at } x=0, \\ -D(\partial c/\partial x) &= 0 \text{ at } x=X. \end{aligned}$$

There is no flow of radioactive  $\text{Cu}^+$  ions from the oxide to the metal ( $x = 0$ ), and, of course, no flow at the oxide-oxygen interface.

Equation (28) may be integrated directly to give:

$$g = A(z + \alpha)^{2(1+\alpha)} e^{-2z}, \quad (29)$$

where  $A$  is a constant of integration, determined by the total amount of radioactive copper present in the oxide.

In our case, only a negligible fraction of radioactive copper will diffuse into the metal; practically all will remain in the oxide.<sup>13</sup> The concentration would, however, follow the same law (Eq. (29)) even if diffusion into the metal were appreciable. The constant  $A$  would then be determined by the fraction of the total amount of radioactive copper in the oxide, which would depend on the diffusion into the metal, as well as on the total amount initially present. Once the quasi-stationary solution is attained, the fractions in the oxide and metal will remain fixed, as there is no further flow from the oxide to the metal.

The final solution may be expressed explicitly as follows:

$$c(x, t) = \frac{A}{t^{1/2}} \left( \frac{x}{X} + \frac{D_0}{D_1} \right)^{2(D_1 + D_0)/D_1} e^{-2x/X}, \quad (30)$$

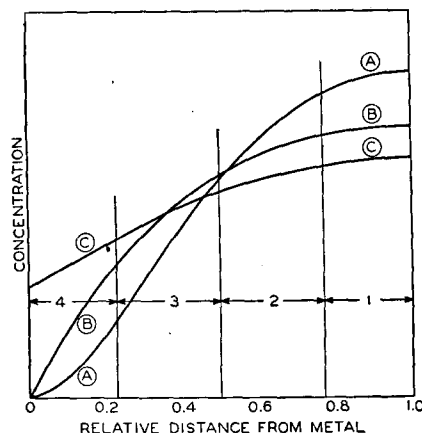


FIG. 2. Calculated concentrations of radioactive copper in oxide layer based on the following assumptions: Curve (A)—(1) self-diffusion takes place only by motion into vacant  $\text{Cu}^+$  ion sites, (2) concentration of vacant sites increases linearly from 0 at the metal interface to a constant value at the oxygen interface ( $\alpha = 0$ ), (3) complete dissociation of centers composed of vacant  $\text{Cu}^+$  sites and defect electrons; Curve (B)—same as (A) except that centers are *undissociated*; Curve (C)—same as (A) except that there is an additional mechanism of diffusion, giving a contribution to the diffusion coefficient independent of position in the oxide, and equal in magnitude to that caused by motion into vacant sites at the oxide-oxygen interface ( $\alpha = 1$ ).

<sup>13</sup> The self-diffusion coefficient of Cu in the metal is of the order  $10^{-9}$  at  $1000^\circ\text{C}$ , as compared with a self-diffusion coefficient of the order  $10^{-7}$ , for Cu in  $\text{Cu}_2\text{O}$  in equilibrium with air at atmospheric pressure and also at  $1000^\circ\text{C}$ .

TABLE III. Calculated and observed values of percent of total activity in successive layers of oxide.  $z$  = fractional distance from metal to oxygen interface.  $D = D_1(\alpha + z)$  = self-diffusion coefficient for  $\text{Cu}^+$  ions. Calculated values of activity are given for different values of  $\alpha$  and for assumptions of both complete dissociation and no dissociation of centers composed of vacant  $\text{Cu}^+$  ion sites and defect electrons.

| Sample | Range of $z$ | Observed | $\alpha = 0$ | Calculated  |      |      |  | Undissoc. $\alpha = 0$ |
|--------|--------------|----------|--------------|-------------|------|------|--|------------------------|
|        |              |          |              | Dissociated | 0.25 | 0.50 |  |                        |
| 1      | 0.77-1.00    | 22.5%    | 21%          | 20%         | 18%  | 17%  |  | 18%                    |
| 2      | 0.50-0.77    | 55.      | 54           | 52%         | 50%  | 46%  |  | 48                     |
| 3      | 0.22-0.50    | 17.5     | 21           | 22%         | 23%  | 25%  |  | 26                     |
| 4      | 0-0.22       | 5.       | 4            | 6%          | 9%   | 12%  |  | 8                      |

with  $D_0$  and  $D_1$  defined by Eqs. (11) and (20), and  $X$ , the thickness of the oxide layer given by (8). In terms of  $D_1$ ,

$$X = 2(D_1 t)^{1/2}. \quad (31)$$

Figure 2 gives a plot of the calculated concentrations of radioactive Cu as a function of the relative distance from the metal for three different assumptions concerning the self-diffusion coefficient:

(A) Complete dissociation of vacant Cu ion sites and defect electrons, and  $D_0 = \alpha = 0$ .

(B) No dissociation of vacant Cu ions sites and defect electrons, and  $D_0 = \alpha = 0$ . This case is discussed briefly in the following section (see Eq. (33)).

(C) Complete dissociation, but with  $D_0 = D_1$ , so that  $\alpha = 1$ .

It is shown in the following section that (A) is in best agreement with experimental data.

## V. COMPARISON OF THEORETICAL AND EXPERIMENTAL VALUES; CONCLUSIONS

Since the thickness of the samples removed by etching were not small compared with the total thickness of the oxide, comparison with theory is best made by using the fraction of the total activity in each sample. If the sample extends from  $z = z_1$  to  $z = z_2$ , the fraction of the total activity to be expected can be obtained by integration of Eq. (27)

$$f = \frac{\int_{z_1}^{z_2} (z + \alpha)^{2(1+\alpha)} e^{-2z} dz}{\int_0^1 (z + \alpha)^{2(1+\alpha)} e^{-2z} dz}. \quad (32)$$

For  $\alpha = 0$ , the integration is elementary. For

$\alpha \neq 0$ , the integrals can be expressed in terms of the incomplete  $\Gamma$  function, for which tables are available.

Table III gives the experimental values of  $f$ , expressed in percentages, as obtained from Table II, and the theoretical values obtained from Eq. (32), for  $\alpha = 0, 0.1, 0.25$ , and  $0.5$ . Complete dissociation of defect electrons and vacant sites is assumed. Good agreement (within the experimental uncertainties) is obtained for  $\alpha = 0$ . The agreement is almost as good for  $\alpha = 0.1$ , but is definitely worse for larger values of  $\alpha$ . Thus we conclude that  $\alpha$  is most probably not greater than about  $0.1$ , and may be considerably smaller.

Results of Wagner and Gr $\ddot{u}$ newald<sup>2</sup> indicate that the fractional concentration of vacant  $\text{Cu}^+$  sites in equilibrium with metallic copper is about  $1.2 \times 10^{-4}$  as compared with about  $17 \times 10^{-4}$  in equilibrium with air at atmospheric pressure, both at  $1000^\circ\text{C}$ . These values would give:

$$\alpha = \frac{1.2 \times 10^{-4}}{17 \times 10^{-4}} = 0.07.$$

Our results are consistent with this value for  $\alpha$ .

Self-diffusion by interchange of  $\text{Cu}^+$  ions in neighboring positions must be small compared with diffusion *via* vacant sites, if it exists at all, under the conditions of our experiment.

Some information can also be obtained concerning the degree of association of defect electrons and vacant  $\text{Cu}^+$  sites. Without more complete data and analysis it is difficult to set limits. If there were complete *association*, the centers would migrate by diffusion alone, so the factor of two would be missing from Eq. (3). The factor of 2 in Eq. (8) would be replaced by  $\sqrt{2}$ . The factor of 2 would also be missing from Eq. (16), and the second term on the right-hand side of Eq. (17) would not appear. The analysis can be carried through for this case, leading to a distribution function for radioactive Cu of the form

$$g(z) = (z + \alpha)^{1+\alpha} e^{-z}. \quad (33)$$

The agreement with observed data is again best for  $\alpha = 0$ , but is not nearly as good as that obtained for the assumption of complete dissociation. Values obtained from integration of Eq.



(33) with  $\alpha=0$  are given in the last column of Table III. We conclude that either

- (a) Dissociation is nearly complete or
- (b) Dissociation is not complete, but the mobility of dissociated centers is much greater than that of undissociated centers.

As far as our results go, they are in complete accord with Wagner's. It is interesting to note

that the numerical agreement between calculated and observed activities is obtained without introducing any empirical constants and without reference to any absolute values for diffusion coefficients or conductivities. The shape of the concentration curve is determined entirely by the mechanisms assumed for the oxidation reaction and for the self-diffusion of radioactive  $\text{Cu}^+$ .

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## A Proposed Interpretation of the Zeta-Potential

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The method used by Gurney and Fowler in explaining the interfacial potential at a metal-solution boundary is applied to the zeta-potential. This gives the  $\zeta$ -potential as a straight line function of the logarithm of the concentration, in agreement with the shape of the curves as found experimentally. To obtain exact agreement between theory and experiment, it is proposed that the dielectric constant of the electrical double layer is about 0.6 that of the value for pure water. This assertion can be checked by accurate measurements on the surface conductance of solution of electrolytes.

### INTRODUCTION

A SATISFACTORY theory correlating the zeta-potential with the concentration of the electrolyte in an aqueous solution has not been devised. Most of the recent attempts at constructing a theory<sup>1</sup> have been used on the idea of the Gouy double layer. The mathematical treatment utilizes solutions of the Poisson-Boltzmann equation

$$\nabla^2\psi = -\frac{4\pi e}{D} \sum_{i=1}^s n_i z_i \exp\left(-\frac{z_i e \psi}{kT}\right), \quad (1)$$

with special boundary conditions. Insufficient and unreliable experimental information has been largely responsible for the failure of most of the attempts. Below, attention is called to a method which is believed to be more fruitful than previous approaches to the problem. Improvements and modifications of this method, in

the light of additional experimental information, will probably yield an adequate theory. The method employed here has been used by Gurney<sup>2</sup> and Fowler<sup>3</sup> in explaining the metallic electrode potential, and by Dole<sup>4</sup> in explaining the glass electrode potential.

Recently significant gains have been made in regard to the experimental knowledge concerning the potential existing at the interface between vitreous silica and aqueous solutions of electrolytes. Hitherto there has been no agreement among the various experimenters<sup>5</sup> in this

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