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INITIAL OXIDATION RATE OF METALS AND THE LOGARITHMIC EQUATION

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ABSTRACT

The logarithmic oxidation equation $y = k_0 \ln (\frac{t}{\tau} + 1)$ is derived assuming control of the rate by electron flow from metal to oxide. Electron flow during oxidation, in turn, is a function of a changing less positive or a more negative space charge in the oxide extending up to several thousand angstrom units from the metal surface, where increasing numbers of trapped electrons at lattice defect sites account for the changing space charge. The space charge is composed of two parts: (1) a uniform charge density layer next to the metal and (2) a diffuse charge density layer beyond the uniform layer. Oxidation follows the logarithmic equation during formation of both space charge layers, but not afterward, with a higher oxidation rate accompanying formation of the diffuse layer. It is shown that under some circumstances the particular distribution of negative charge in the diffuse layer may lead to the cubic oxidation equation. Experimental conditions, especially impurities present in the oxide and its heat treatment, probably determine which electric charge distribution is favored. For oxidation beyond the space charge layer, either the linear equation is obeyed, with control of the rate still focussed at the metal-oxide interface, or, more frequently, the parabolic equation is obeyed with control centered in diffusion and migration processes in the oxide, in accord with Wagner's theory.

From oxidation data for copper, the density of trapped electrons

in the uniform charge density Cu_2O layer at 150° is calculated to be 1.3×10^{15} which decreases to 6×10^{13} at 250°C. The number of available sites for trapped electrons in the diffuse layer is calculated correspondingly to be 1.0×10^{14} and 2.6×10^{12} respectively. The thickness of the uniform charge density layer varies from 360 Å at 150° to 1630 Å at 250°C.

The Rideal-Jones empirical relation $\Delta E = \phi - 3.6$, where ΔE is the activation energy for oxidation and ϕ the metal work function, both in electron volts, and which has been shown to hold for carbon, tungsten and platinum is shown herewith to apply to nickel, tantalum and titanium, and more approximately to copper and iron. This relation is derived theoretically from the same fundamental assumptions used in deriving the logarithmic oxidation equation.

INITIAL OXIDATION RATE OF METALS AND THE LOGARITHMIC EQUATION

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Whenever the oxidation rate of a metal is controlled by diffusion of ions (or lattice vacancies) and by migration of electrons (or positive holes) through the oxide film, the familiar parabolic equation applies:

$$y^2 = k_1t + C \tag{1}$$

where y is the thickness of the film, t is time, and k_1 and C are constants. (C may sometimes be zero.) Wagner$^{(1)}$ established the fundamental reaction kinetics for this equation and was able to calculate the rate constant k, and its dependence on oxygen partial pressure, from independent physical chemical properties of oxide and metal.

However, oxidation in the lower temperature range or when thin films are formed is found to follow the so-called logarithmic equation:

$$y = k_o \ln \left(\frac{t}{\tau} + 1\right) \tag{2}$$

where k_o and τ are constants. For $t \gg \tau$, this equation is approximated by:

$$y = k_o \ln t - k_o \ln \tau \tag{3}$$

and y becomes linear plotted with logarithm of t.

When the logarithmic equation was first announced in 1922 by Tammann

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(1) C. Wagner, Z. physik. Chem., 21B, 25 (1933); 32B, 447 (1936); 40B, 455 (1938).

and Köster(2) on empirical grounds, its validity was questioned. However, careful measurements since then have established beyond doubt that for oxidation of many metals under specific conditions of temperature and time, this equation and no other describes the facts. The logarithmic equation, for example, has been shown to apply to oxidation of copper(2,3,4,5,6), zinc(2,7), cadmium(2), lead(2), tin(2), manganese(2), iron(2,8,9,10,11), nickel(2,12,13), aluminum(3,14), titanium(15), and tantalum(16).

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(2) G. Tammann and W. Köster, Z. Anorg. Allg. Chem., 123, 196 (1922).

(3) B. Lustman and R. Mehl, Trans. AIME, 143, 246 (1941).

(4) A. H. White and L. Germer, Trans. Electrochem. Soc., 81, 305 (1942).

(5) H. H. Uhlig and A. Brenner, Acta Metallurgica, 3, 108 (1955).

(6) R. Tylecote, J. Inst. Metals, 78, 327 (1950).

(7) W. Vernon, E. Akeroyd and E. Stroud, J. Inst. Metals, 65, 301 (1939).

(8) B. Lustman, Trans. Electrochem. Soc., 81, 359 (1942).

(9) A. Winterbottom, J. Iron and Steel Inst., 165, 9 (1950).

(10) W. Vernon, E. Calnan, C. Clews and T. Nurse, Proc. Royal Soc., 216A, 375 (1953).

(11) D. Davies, U. Evans and J. Agar, Proc. Royal Soc., 225A, 443 (1954).

(12) H. H. Uhlig and J. J. Pickett, unpublished data.

(13) W. Scheuble, Z. Physik., 135, 125 (1953).

(14) A. Steinheil, Ann. Physik., 19, 455 (1934).

(15) J. Waber, G. Sturdy and E. Wise, JACS, 75, 2269 (1953).

(16) J. Waber, G. Sturdy, E. Wise and C. Tipton, J. Electrochem. Soc., 99, 121 (1952).

Several attempts have been made to describe a mechanism of diffusion through oxides resulting in the logarithmic equation, such as by assumed specialized flaw-paths or zones of loose structure in oxides(17), or by diffusion blocks and leakage paths in the oxide(11,18), or by an assumed ion concentration gradient or polarization(19)*. Mott(20) contributed an analysis of

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(17) U. R. Evans, Trans. Electrochem. Soc., 83, 335 (1943).

(18) U. R. Evans, Nature, 157, 732 (1946).

(19) H. Miley, Trans. Electrochem. Soc., 81, 391 (1942).
O. Hamilton and H. Miley, Ibid, 81, 413 (1942).

(20) N. Mott, Trans. Faraday Soc., 35, 1175 (1939).

*Vernon, Calnan, Clews and Nurse(10) believe that the logarithmic equation, as found to apply to thin film oxidation of iron, expresses oxygen diffusion through the oxide to the metal surface, whereas the parabolic equation, when it applies, corresponds to diffusion of iron ions through the oxide from metal to gas. They base their opinion on observed greater weight gain of iron specimens when oxidized in the logarithmic rate region then corresponds to oxygen in the isolated oxide film, in contrast to correspondence of weight gain and oxygen in the oxide in the parabolic region. Their observations, however, can be explained by surface oxidation of carbon contained in their iron (0.09% C), occurring parallel with the oxidation of iron, the carbon oxidation products being retained by the iron oxides perhaps as carbonates. For higher temperatures and thicker oxide films where the parabolic equation holds, carbonates are not stable and, hence, are not expected to be retained by the film. Oxidation of carbon also explains the delayed appearance of interference colors which they report. In this connection, the effect of carbon probably enters as a factor in the thinning (by reduction) of oxide films on iron during vacuum treatment reported by Davies, Evans and Agar(11). A pertinent reference in this regard is the work of V. Holm(21).

(21) V. Holm, J. Res. Nat. Bur. Stds., 28, 569 (1942).

electronic and ionic processes in thin insulating oxide films of stoichiometric composition on metals which led to a logarithmic equation. He employed the tunnel effect of quantum mechanics to express rate of electron flow from metal to oxide which he assumed controlled the oxidation process. This special model accounted, however, for oxide films only in the order of 40 Å, whereas the general logarithmic equation in practice holds for films as thick as 10,000 Å, and also his derivation predicted a temperature independent k_o, contrary to what is observed. Subsequently, Mott and Cabrera(22,23) hypothesized an alternative rate control by diffusion of metal ions rather than escape of electrons, assuming that negatively charged oxygen ions when adsorbed on the oxide surface create an electric field within the oxide which induces migration of positive ions to the oxide surface. They showed that under conditions where migration velocity of positive ions is proportional to field strength, a parabolic oxidation equation results, but for thinner films for which the migration velocity is proportional to an exponential power of the field strength and rate of escape of metal ions into the oxide becomes controlling, an equation of the type $\frac{1}{y} = C - k \ln t$ is derived (the inverse logarithmic equation). This also led to the situation where below a critical temperature, a limiting oxide film thickness could be expected. But the logarithmic equation (2) observed experimentally did not result from these particular assumptions.

Campbell and Thomas(24) expressed the opinion that initial deviations

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(22) N. Mott, Trans. Faraday Soc., 43, 429 (1947).

(23) N. Cabrera and N. Mott, Reports on Prog. in Physics, 12, 163 (1949).

(24) W. Campbell and U. Thomas, Trans. Electrochem. Soc., 91, 623 (1947).

from the parabolic equation of oxidation for copper are caused by a space charge layer in the oxide about 10^4 Å thick as determined by electrical capacitance. Tylecote(6) confirmed that the logarithmic equation holds for films less than about 10^5 Å thick, whereas the parabolic equation applies to thicker films. Later discussion in ~~this~~ the present paper bears out that the logarithmic equation is related to conditions applying ~~during~~ to formation of the space charge layer, and that the mechanism of oxidation changes for thicker oxide films.

Oxidation Control at the Metal-Oxide Interface

It is perhaps obvious that an acceptable mechanism of thin film oxidation of metals should first establish the actual rate controlling process. A detailed examination of reaction-rate data provides evidence that the rate is controlled largely by processes at the metal-oxide interface rather than by reactions at the oxide-oxygen interface, or by diffusion through the oxide. This evidence comes from the effect on the oxidation rate of:

(1) crystal orientation, one crystal face oxidizing at a rate appreciably different from any other crystal face(3,8,25). Lustman(8), and Mehl and McCandless(26) pointed out that these differences cannot be ascribed to differing diffusion rates through oxides specifically oriented on metal crystal faces, because the oxides of iron and copper at low temperatures are cubic, and diffusion through cubic lattices is

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(25) A. Gwathmey, "Corrosion Handbook", p. 33-35, edited by H. H. Uhlig, John Wiley and Sons, Inc., New York, 1948.

(26) R. Mehl and E. McCandless, Trans. A.I.M.E., 125, 531 (1937).

isotropic. Differing degree of sintering or differing recrystallization of oxide as a function of crystal face is also not an acceptable explanation, because Mehl, McCandless and Rhines(27) found that oxides grown on single crystals of copper remain single crystals even after they have developed into thick scales, precluding the possibility of any sintering or recrystallization.

(2) Lattice Transformation

The activation energy for oxidation of iron in CO_2 + H_2O undergoes a discontinuity at the transformation temperature of iron from α (bcc) to γ (fcc) lattice(28). A similar discontinuity was found for a 10.6% chromium-iron alloy(29), heated in oxygen under conditions where thin films are formed.

(3) Curie Temperature

The activation energies for oxidation of several chromium-iron alloys in oxygen are higher above the Curie temperatures than below(29). This relation is also found to hold for nickel(12). Tammann and Siebel(30) furthermore found discontinuities in the oxidation rates of iron-nickel alloys at the Curie temperatures. All these observations

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(27) R. Mehl, E. McCandless and F. Rhines, Nature, 134, 1009 (1934).

(28) K. Fischbeck and F. Salzer, Metallwirtschaft, 14, 753 (1935).

(29) H. H. Uhlig and A. S. Brasunas, J. Electrochem. Soc., 97, 448 (1950).

(30) G. Tammann and G. Siebel, Z. anorg. allg. Chem., 148, 297 (1925).

show that magnetic transitions in metals at the Curie temperature can affect the oxidation rate.

The overall evidence for control of rate at the metal-oxide interface applies whenever thin films are formed. For thicker films, of course, where diffusion through the oxide is controlling, factors of grain orientation, lattice transformation and magnetic change are no longer important.

Control by Electron Emission

Mott(22,23) favored slow escape of metal ions from the metal into the oxide lattice on the controlling step in several reactions producing relatively thin films, and electron emission as controlling in insulator type films below 40 Å thick. Convincing evidence is available to show that actually electron flow from metal to oxide is the slow step for several metals, and therefore dominates the reaction process in formation of films as thick as several thousand Angstroms. This evidence in part comes from the empirical relation first proposed by Rideal and Wansbrough-Jones(31).

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(31)E. Rideal and O. Wansbrough-Jones, Proc. Royal Soc., 123A, 202 (1929).

They showed that for oxidation of platinum, carbon and tungsten the following relation holds:

$$\Delta E = \phi_o - K \qquad (4)$$

where ΔE is the observed activation energy for oxidation, and ϕ_o is the work function of the metal or carbon. The term K is a constant equal to 3.6 electron volts (83 kcal), and was expressed by Rideal and Wansbrough-Jones as the sum of $\phi_a + \phi_e$ where ϕ_a is the energy of adsorption and ϕ_e is the electron affinity of the adsorbed oxygen molecule. In other words, for these elements, each of whose oxides at elevated temperatures is volatile, the activation energy for oxidation is related directly to the energy necessary to transfer an electron from metal to oxygen.

According to Eq. (4), metals with work function less than 3.6 electron volts (e.g., Na and Ca) possess an activation energy for oxidation equal to zero (it cannot be negative), and the metal oxidizes initially as rapidly as oxygen comes into contact. For metals of higher work function, on the other hand, (e.g., Ni, Pt, W), the activation energy is positive, the reaction is delayed, and more oxygen reaches the metal surface than can react. This means that oxygen is able to adsorb (chemisorb) on the metal, for which it has a certain affinity, remaining there a measurable time before metal atoms leave their lattice to initiate an oxide lattice.

It is of interest to note that the measured value of K in Eq. (4) (3.6 e.v.) approximates the electron affinity of the oxygen atom (3.4 e.v.)(32). The small difference of about 0.2 electron volt (4600 cal.) is possibly accounted for by the sum of energy changes associated with adsorption and dissociation of molecular oxygen on the metal surface. In other words, the slow process of oxidation of carbon, Pt and W can be interpreted as the transformation of physically adsorbed molecular oxygen, in which only weak Van der Waals binding forces apply, to chemisorbed atomic oxygen with the metal acting as electron donor and oxygen as electron acceptor. Accordingly, equation (4) indicates that both rates of physical adsorption of oxygen on the metal surface and volatilization of the metal-oxygen ion complex, at the high temperatures presently considered, are rapid compared to chemisorption

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(32) "Oxidation Potentials", W. M. Latimer, second edition, p. 18, Prentice-Hall, Inc., New York, 1952.

of oxygen. This conclusion is in agreement with previous expressions to the effect that chemisorption is often (but not always) a slow process requiring an activation energy(33,34). It also agrees with previous proposals that the process of physical adsorption precedes chemisorption(35,36).

It is significant that the Rideal-Jones relation can be applied also to some metals having non-volatile oxides under conditions where the oxide films are thin and the logarithmic equation is obeyed. The data are summarized in Table I, and provide evidence that for such metals oxidation continues to be controlled by electron flow from the metal. Presumably, the energy gained by the electron entering the oxide is almost exactly compensated for by the electron leaving the oxide again at the oxide-air interface to enter the oxygen atom, now adsorbed not on the metal, but on the oxide. The negatively charged oxygen ions eventually enter lattice positions in the oxide in accord with the Wagner mechanism of oxidation and tarnish. Therefore, ΔE is again given essentially by the difference of the metal work function and the electron affinity of oxygen. From the above considerations, Eq. (4) can be expected to hold whenever electron escape from the metal controls, and when the work function of the oxide has approximately the same value at the metal-oxide and oxide-environment interfaces.

The observed relation between work function and activation energy

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(33) H. S. Taylor, J.A.C.S., 53, 578 (1931).

(34) "Chemisorption", B. Trapnell, Academic Press, New York, 1955.

(35) J. Becker and C. Hartman, J. Phys. Chem., 57, 153 (1953).

(36) G. Ehrlich, J. Phys. Chem., 59, 473 (1955).

TABLE I

RELATION BETWEEN ACTIVATION ENERGY FOR OXIDATION AND WORK FUNCTION: $\Delta E = \phi_0 - K$

	ΔE	ϕ_0	K
Pt	2.74 e.v.	6.35 e.v.*	3.61 e.v.
W	0.87	4.48*	3.61
C	0.52	4.31*	3.79
Ni	0.90 ■	4.50**	3.60
Ta	0.55 ▲	4.12***	3.57
Ti	0.56 ●	3.95**	3.39

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*These values employed by Rideal and Wansbrough-Jones are close to mean values given by H. Michaelson based on a review of the literature, with the exception of platinum where the value in Table I, employing photoelectric data of DuBridge (1928) is 1.06 volt higher.

■ H. H. Uhlig and J. J. Pickett, unpublished data.

▲ Reference 16.

● Reference 15

**(37) K. Krishnan and S. Jain, Nature, 170, 759 (1952).

***(38) H. Michaelson, J. Applied Physics, 21, 536 (1950).

clarifies why the rate of oxidation should vary with crystal face, since the work function also varies with crystal face(39,40,41). Furthermore, the work function of γ iron differs from that of α iron, in accord with change of activation energy for oxidation above and below the transition temperature. Houdremont and Rädiger(42) reported a higher work function for γ than for α iron, but Wahlin(43) reported the reverse, namely, a higher value for α than for γ iron*.

Along the same lines, values of work function ϕ_0 for nickel above the Curie temperature (350°C) are higher than values below the Curie temperature(44) corresponding to an observed activation energy for oxidation of nickel in oxygen above the Curie temperature that is 1150 calories/mole, or 0.05 e.v. greater than the value below the Curie temperature (12). These correlations

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(39) R. Smoluchowski, Phys. Rev., 60, 661 (1941).

(40) H. Farnsworth and R. Winch, Phys. Rev., 58, 812 (1940).

(41) Also various papers on field emission microscope, e.g., E. W. Müller, Ergeb. der Exakten Naturwiss., 27, 290-360 (1953); J. A. Becker, Bell Syst. Tech. J., 30, 907 (1951).

(42) E. Houdremont and O. Rüdiger, Naturwiss., 39, 399 (1952).

(43) H. Wahlin, Phys. Rev., 61, 509 (1942).

(44) A. Cardwell, Phys. Rev., 76, 125 (1949).

*The activation energy for oxidation is higher above the γ-α transition temperature.

point toward the important part played by electron flow from the metal in the initial oxidation process, and focus the necessity of attention on various factors affecting electron emission during oxide growth.

Space Charge Effects

If at equilibrium, an oxide has greater electron affinity or higher work function than the metal in contact from which it forms, the oxide will tend to acquire excess negative charge, and the metal, in turn, will acquire an equal positive charge, resulting in an electrical double layer. Similarly, if the electron affinities are reversed, the oxide will lose electrons to the metal. The amount of charge eventually transferred across the boundary in either event will set up a field compensating exactly for the differences in electron affinity of the two phases. Or stated another way, when contact is made between a metal and a semi-conductor, all the electronic energy levels of the semi-conductor are altered relative to those of the metal by the amount of the contact potential difference.

For two dissimilar metals in contact, the electric charge constituting the double layer is confined to a very small region of atomic dimensions at the interface. In semi-conducting oxides, on the other hand, with filled energy levels and relatively few electrons excited into the conduction band, excess charge associates itself mainly at lattice imperfections, such as occur at impurity centers or at lattice vacancies. Negative charge of this kind exists as so-called bound or "trapped" electrons(45). Similarly, bound or trapped electron-deficient sites or positive holes may exist. In

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(45) N. Mott and R. Gurney, "Electronic Processes in Ionic Crystals", pp. 80-88, Oxford Press (1940).

view of the restricted number of sites for trapped electrons or positive holes, the space charge in oxides extends over a greater volume than in the case of metals. Volta or contact potential measurements for oxidized copper and zinc, as described later, indicate that the space charge may extend into the oxide film for several thousand Angstroms. When the oxidation rate, therefore, is controlled by electron flow from the metal, an increasing negative space charge (or decreasing positive space charge) obviously enters as an important factor in establishing the rate of electron flow, tending in general to slow down escape of electrons as the oxide grows, and, therefore, simultaneously slowing down escape of metal ions and the oxidation process itself.

Volta Potential Measurements and the Initial Oxidation Reaction

The oxidation process, of course, is not an equilibrium situation, but rather a dynamic building up of oxide through interaction of the metal and oxide with molecular oxygen. The various steps in the initial process appear to be:

(1) rapid physical adsorption of molecular oxygen on the metal

(2) dissociation of molecular oxygen into chemisorbed atomic oxygen

(3) sublimation of the metal-oxygen complex to initiate an oxide lattice

(4) vaporization of metal ions and electrons into the oxide to form additional oxide

(5) formation of lattice vacancies by oxygen, or combination of interstitial metal ions with oxygen at the oxide-air interface. (We shall not treat the relatively few known cases where oxygen diffuses to the metal-oxide interface.)

If step 4 controls, in accord with present considerations, the rate of escape of ions is given by the expression $K' \exp\frac{-W}{kT}$, where W is the heat of sublimation of the ions from the metal into the oxide at the metal-oxide interface, k is Boltzmann's constant, T is the absolute temperature, and K' is a constant. Electrons can be assumed to evaporate simultaneously at a rate equal to $K'' \exp\frac{-e\phi}{kT}$, where ϕ is the work function of the metal as modified by the oxide in contact. When electron emission is the slower process and therefore the controlling factor in the formation of oxide, as has been discussed, and since the exponential terms and not K' and K" in the above rate expressions are usually dominant, it follows that ϕ in this instance must be greater than W.

This state of affairs leads to an initial positive space charge in the oxide when a metal is first oxidized because of the rapid escape of positive metal ions. Their rate of escape almost immediately is established by the slower electron flow from metal to oxide. As the oxide grows, a decrease of positive space charge occurs because a portion of the electrons escaping into the oxide become trapped at oxide lattice imperfections. Eventually, the oxide may acquire an overall negative charge depending on the final equilibrium state of electric charge.

As oxidation continues, rate of escape of ions and of electrons approach each other, and some factor other than electron flow assumes control of the rate, particularly after the oxide grows to a thickness corresponding to equilibrium electric charge distribution at the metal-oxide interface (or when the Fermi levels in metal and oxide become identical). Thicker oxides forming beyond the boundaries of the space charge layer are electrically neutral. If escape of electrons and ions should continue to control the rate at this stage, as is possible, the oxidation rate would become constant, leading to the so-called linear equation, ($y = k_2t + c_3$). But the constant oxidation rate in this instance would be preceded by an initially more rapid and gradually decreasing rate. Gulbransen and Wysong(46) found aluminum to behave somewhat along these lines which may confirm that this type of oxidation control is sometimes found. Aluminum when oxidised in low pressure oxygen below 450°C followed the parabolic equation, and above 450°C followed the linear equation. Whether one equation or another is obeyed probably depends on the defect structure of the oxide under the particular conditions of any given experiment. That is, factors become important which determine whether sites continue to be available, as the oxide grows, for trapping of electrons or positive holes, and which establish whether control of the rate remains at the metal-oxide interface or is transferred to diffusion and conduction processes in the oxide. Also, patterns of crack formation in the oxide may play a role in accord with the conventional explanation of mechanism applied to the linear equation. Nevertheless, it is apparent that the linear equation, as described above, may also hold for metals covered by a continuous protective oxide film <u>free of cracks</u>. Such protective films have, in fact, been observed when magnesium, which follows the linear equation, oxidises initially(47,48).

Also, the black crustaceous MgO found by Leontis and Rhines(47) next to the

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(46) E. Gulbransen and W. Wysong, J. Phys. Chem., <u>51</u>, 1087 (1947).

(47) T. Leontis and F. Rhines, Trans. AIME, <u>166</u>, 265 (1946).

(48) E. Gulbransen, Trans. Electrochem. Soc., <u>87</u>, 589 (1945).

metal surface, over which white MgO forms, may be visible evidence of the space charge layer, as well as evidence, as they suggest, of a non-stoichiometric composition.

Evidence for the trend of space charge with oxide growth is provided by contact or Volta potential measurements of metals undergoing oxidation in air at elevated temperatures. Typical potentials of copper oxidized in air at 225°C and of zinc at 200°C are given in Figs. 1 and 2. These measurements were made employing the vibrating condenser method(49,50). A silver electrode as reference was heated electrically to the same temperature as the copper or zinc electrodes, all of the same size (1 x 1"), the temperature of the electrodes being measured and controlled automatically by means of embedded thermocouples. The initial oxidation process for copper results in a Volta potential 0.5-0.7 volt more active than silver, and for zinc about 1.5 volt more active than silver, corresponding to buildup of a positive space charge in the metal oxides. As the metals oxidize further, these potentials become first rapidly more noble (more like Ag), indicating that the positive space charge is being neutralized, followed by a less rapid and prolonged trend in the noble direction.

Similar conclusions may be derived from Volta potential measurements reported by Hirschberg and Lange(51). They heated zinc surfaces between

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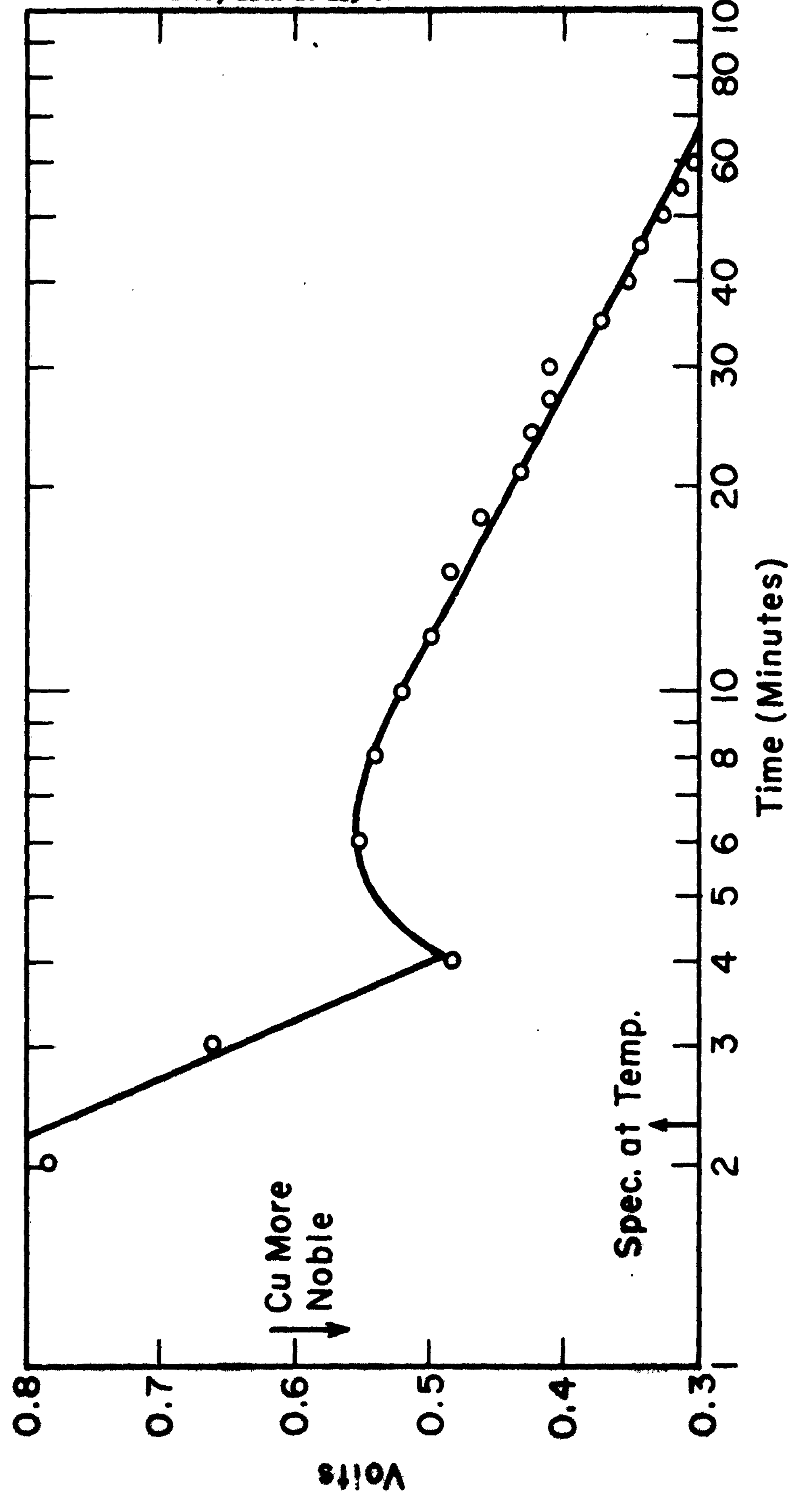
(49) W. Zisman, Rev. Sci. Instr., 3, 367 (1932).

(50) H. H. Uhlig, J. Applied Phys., 22, 1399 (1951).

(51) R. Hirschberg and E. Lange, Naturwissenschaften, 39, 187 (1952).

Fig. 1 Volta Potentials of Copper Oxidizing in Air, vs Silver, Both at 225°C.



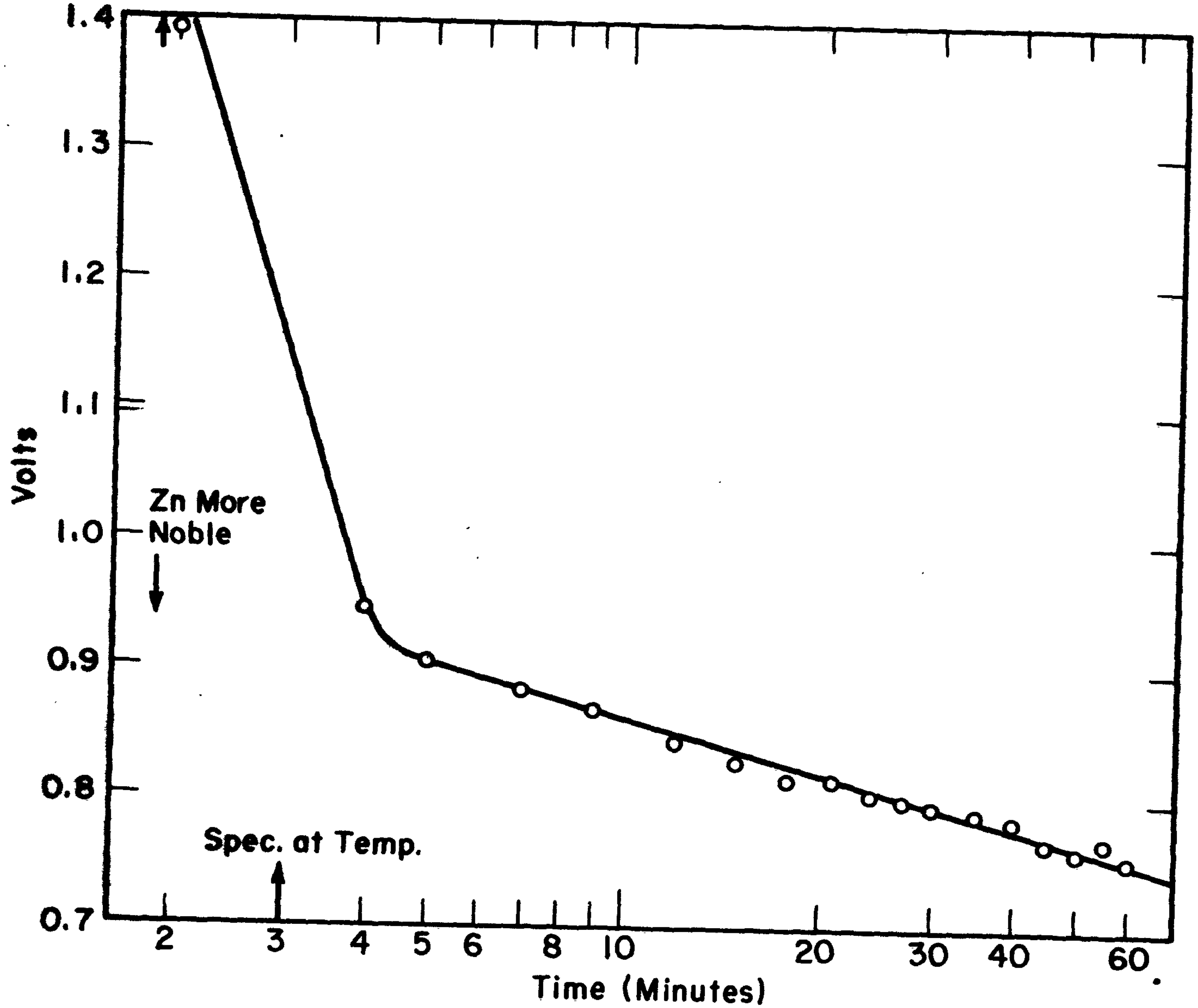


Fig. 2 Volta Potentials of Zinc Oxidizing in Air, vs Silver, Both at 200°C.

20 and 407°C for 20 minutes at each temperature, and measured Volta potentials of such surfaces (presumably at room temperature rather than at elevated temperature as above) with respect to zinc. At lower temperatures of oxidation and hence for the thinner films, the sign of Volta potential corresponded to a positive space charge in the oxide, but for higher temperatures and thicker oxide films the sign reversed.

Volta potential measurements of metals undergoing oxidation are not easily reproducible, so that quantitative features of Figs. 1 and 2 should not assume great weight. Qualitatively, however, the trend of effects can be reproduced from one run to the next. These measurements are being continued at various temperatures and for various metals and will be reported elsewhere. In all instances observed so far, the sign of Volta potential after an initial period of oxidation, corresponds to decreasing positive space charge or increasing negative charge. Interpretation of Volta potential measurements as described above assumes that electric charge at the air-oxide interface remains essentially constant, which is a reasonable assumption for constant partial pressure of oxygen; and that major change of potential is accounted for by changing electric charge in the thin oxide films.

The potential at the metal-oxide interface set up by changing space charge in the oxide layer alters, of course, the work necessary to carry a positive ion or electron across the interface, and, hence, influences their rate of escape into the oxide. It is this approach to the oxidation process that is explored next.

Calculation of Oxidation Rate

We shall consider first that excess charge in the growing oxide film of total thickness y is uniformly distributed throughout the oxide volume. This corresponds to an oxide with uniform defect or impurity density at which electrons or positive holes are bound. When a film of this kind reaches a supposed thickness ℓ, we shall further assume that the total negative charge in the film creates a field at the metal surface compensating exactly for the positive field. The positive field results from excess metal ions of positive charge escaping into the oxide, or, alternatively, results from the electron "sink" at lattice vacancies formed at the outer oxide surface. Therefore, when the hypothetical film thickness becomes ℓ, the electric field at the metal surface reaches the equilibrium value of zero (Fermi levels in oxide and metal are equal), corresponding to an order of film thickness beyond which the space charge can exert either a constant or a negligible effect on electron escape and rate of oxide growth. If n is the density of trapped electrons in the oxide, and -e is the charge on the electron, the potential V at the metal-oxide interface is given by Poisson's relation:

$$\frac{d^2V}{dy^2} = \frac{4\pi ne}{\epsilon} \qquad (5)$$

where ϵ is the dielectric constant of the oxide, and ~~Considering~~ the term y is ~~to be~~ the total oxide thickness at any given time, then integrating (5) we have:

$$\frac{dV}{dy} = \frac{4\pi ne}{\epsilon} y + C_1 \qquad (6)$$

Since the field dV/dy equals zero at the metal surface when the assumed thickness of the constant charge density film is ℓ, it follows that

$C = \frac{-4\pi ne\ell}{\epsilon}$ and

$$V = \frac{-4\pi ne}{\epsilon}\left(\ell y - \frac{y^2}{2}\right) + C_2 \qquad (7)$$

Now the potential at the metal surface is $-(\phi - v)$ for the condition that the oxide film thickness y approaches zero, where e ϕ is the energy required to remove an electron from the metal and place it in the oxide at the metal-oxide interface, and v is the apparent positive potential at the metal surface created by the growing oxide. The term v, in general, is numerically equal to the potential difference between the metal-oxide interface and the oxide-oxygen interface for metal-oxide systems in which lattice diffusion of oxygen ions toward the metal is negligible. As will be shown later, v is approximated by the electron affinity of oxygen adsorbed on the oxide; it is, therefore, a constant independent of oxide thickness and, like the work function, it is substantially independent of temperature. Then $C_2 = -(\phi - v)$.

For values of y much smaller than ℓ, the term $y^2/2$ can be neglected. Hence, from Eq. (7), the potential affecting escape of an electron from the metal surface in contact with an oxide of increasing uniform negative space charge is approximated by:

$$V = \frac{-4\pi ne}{\epsilon} \ell y - (\phi - v) \tag{8}$$

Rate of oxide growth dy/dt is proportional to rate of escape of positive ions, which in turn is controlled by rate of electron escape. Electron current across the contact of a metal and a semi-conducting oxide is found to follow an equation of the type(52):

$$i = A' \exp \frac{-e\phi}{kT} \left(\exp \frac{e v'}{kT} - 1\right) \tag{9}$$

where A' is a constant, ϕ is the work function of the metal modified by

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(52) "Crystal Rectifiers", H. Torrey and C. Whitmer, p. 22, 80-84, McGraw-Hill, New York, 1948.

contact with the oxide, and v' is the applied voltage across the metal-oxide interface. The above equation satisfactorily describes the observation that log i for a rectifying contact is linear with v' over a limited range of applied voltage. Since in our present considerations, v' is found to be in the order of volts, the term $\exp \frac{e\,v'}{kT}$ is much greater than unity (at 1 volt, 25°C, $\frac{e\,v'}{kT} = 39$), and, hence, equation (9) simplifies to

$$i = A' \exp \frac{-e\,(\phi - v')}{k\,T} \qquad (10)$$

This equation neglects the reverse electron current from oxide to metal and considers as important only current leaving the metal*. A simplification of this kind is justified by the high positive field at the metal surface when a metal first oxidizes and whenever the oxide film is relatively thin. Then since the rate of film growth is proportional to electron flow, $\frac{dy}{dt} = \beta i$, where β is a constant, and employing Eq. (8) for the actual potential at the metal surface, i.e., substituting $v - \frac{4\,\pi\,ne}{\epsilon}\,\ell\,y$ for v', we have:

$$\frac{dy}{dt} = A \exp \frac{-e\phi + ev - \frac{4\pi\,ne^2\,\ell\,y}{\epsilon}}{k\,T} \qquad (11)$$

where A now replaces $A'\beta$. This equation implies that the effective applied voltage v across the metal oxide surface is decreased by the accumulating negative charge in the oxide as the oxide grows. Integrating on the condition that when $y = 0$, $t = 0$:

$$y = \frac{\epsilon\;kT}{4\,\pi\,ne^2\,\ell} \ln \left[\left(\frac{4\,\pi\,ne^2\,\ell\,A}{\epsilon\;kT} \exp \frac{-e(\phi - v)}{kT}\right)t + 1\right] \qquad (12)$$

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*Eq. (10) applies in theory only to electron current leaving the metal and entering the oxide when this is the direction of easy flow or forward direction, as is the case when copper oxidizes. Oxidation of zinc, to the contrary, corresponds to electron flow in the blocking direction, but even here current-voltage data for rectifying contacts indicate that an equation applies of the same form as (9) ~~without alteration in sign of the applied voltage~~, but with values of A' and ϕ differing from corresponding values for current flow in the forward direction. See Ref. 52, p. 84-85 which is the same form as the logarithmic equation observed experimentally, namely:

$$y = k_o \ln \left(\frac{t}{\tau} + 1\right) \qquad (13)$$

where $k_o = \frac{\epsilon kT}{4 \pi n e^2 \ell}$ and $\tau = \frac{\epsilon kT}{4 \pi n e^2 \ell A} \exp \frac{e(\phi - v)}{kT} = \frac{k_o}{A} \exp \frac{e(\phi - v)}{kT}$

The above equation (12) applies only to a limited film thickness adjacent to the metal. At the stage of oxidation where the existing interface electric field and oxide structure are no longer conducive to filling all available sites for trapped charge in the oxide, the available sites become only partially occupied. Hence, the excess charge density in oxide further removed from the metal is no longer saturated and uniform but is influenced by the potential existing at any point in the film. On this premise, non-uniform charge density becomes a property of films that are thicker than those considered above. The situation is similar to the diffuse double layer at metal surfaces in contact with electrolytes, as described by Gouy(53), Chapman(54) and Stern(55). For oxide films still thicker than the diffuse barrier layer, the space charge disappears, and the oxide becomes electrically neutral.

When the charge density in the oxide depends on potential V, the density of positive charge in accord with the derivation of Mott and Gurney(56)

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(53) G. Gouy, J. de Physique, 9, 457 (1910).

(54) D. Chapman, Phil. Mag., 25, 475 (1913).

(55) O. Stern, Z. Elektrochem., 30, 508 (1924).

(56) Ref. 45, p. 276.

can be expressed by $n_1 \exp \frac{-eV}{kT}$, and the corresponding density of negative charge by $n_2 \exp \frac{eV}{kT}$ where n_1 and n_2 respectively represent the density of lattice sites at which positive and negative charge may attach itself. The excess negative charge density n is the difference of these expressions, and assuming $n_1 = n_2 = n_o$

$$n = n_o \left(\exp \frac{eV}{kT} - \exp \frac{-eV}{kT}\right) \qquad (14)$$

If the energy eV is small compared with kT, the exponential terms can be expanded neglecting higher power terms than the first, whereupon

$$n = \frac{2\, n_o\, eV}{kT} \qquad (15)$$

Substituting this expression for n into the Poisson equation and assuming the potential to be zero when the field is zero, and $V = C_1$ at $Y = 0$, where Y marks the distance into the diffuse charge density layer:

$$V = C_1 \exp \frac{-2Y}{x_o} \text{ and } n = \frac{2\, n_o\, e\, C_1}{kT} \exp \frac{-2Y}{x_o}$$

where x_o is equal to $\left(\frac{\epsilon\, k\, T}{2\, \pi\, n_o\, e^2}\right)^{\frac{1}{2}}$, and C_1 is the potential at the oxide-oxygen interface corresponding to the oxide thickness L marking a transition between uniform and diffuse charge density. The density of negative charge n obviously falls off rapidly with distance Y into the oxide (Fig. 3). If we now consider the potential at the metal-oxide interface produced by the diffuse space charge, potential V must become more negative with increased <u>total</u> thickness of oxide y, following an equation identical with the above, except for sign of the exponent and where C_1 is replaced by C_o equal to the potential at the oxide-metal interface when $y = 0$. If we assume for simplicity that $y = 0$ when the thickness of oxide is L corresponding to a transition from uniform to diffuse charge density, then from

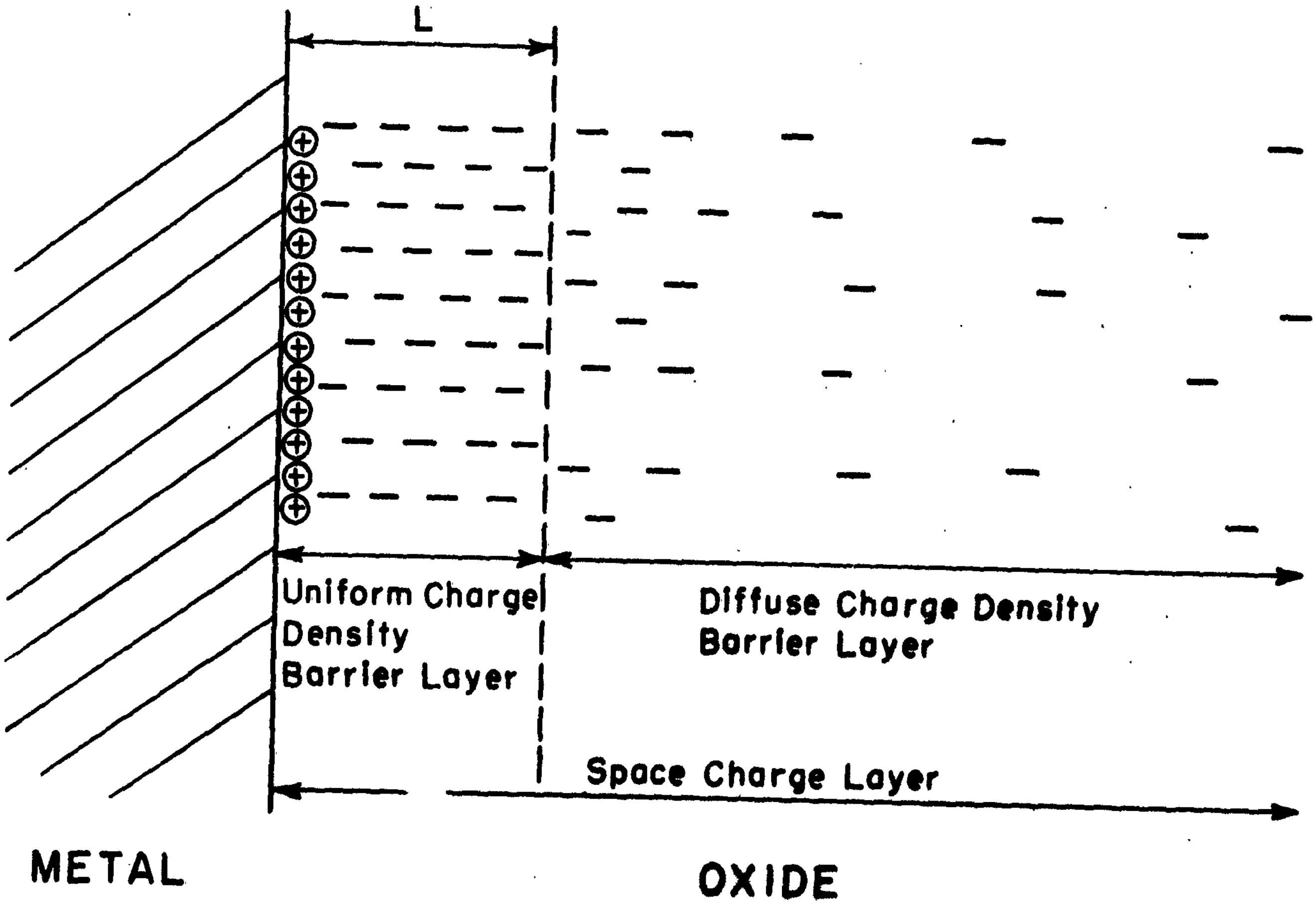

Fig. 3 Schematic Diagram of Trapped Negative Charge in Uniform and Diffuse Barrier Layers. Positive charge may be localized as shown, or distributed throughout a larger volume of oxide.

Eq. (8):

$$C_o = \frac{-4\pi n e \ell L}{\epsilon} - (\phi - v) \qquad (16)$$

The oxidation rate as before is proportional to the number of electrons escaping from the metal into the oxide per unit time. From Eq. (10) and (16), and the relation: $V = C_o \exp \frac{2y}{x_o}$, the oxidation rate is given by the following expression:

$$\frac{dy}{dt} = A \exp \frac{C_o e \exp \frac{2y}{x_o}}{kT} \qquad (17)$$

Furthermore, on the condition that $y \ll \frac{x_o}{2}$, the term $\exp \frac{2y}{x_o}$ can be expanded and approximated by $1 + \frac{2y}{x_o}$. As will be shown later, n_o for Cu_2O at 225°C equals 4.9×10^{12}, $\epsilon = 10.5$, and $\frac{x_o}{2}$, therefore, equals 16,000 Å. This thickness is measured not from the metal surface, but from the point at which the oxide grows beyond uniform density of negative charge; it is appreciably larger than values of oxide thickness y with which we are presently concerned, and on this basis expansion of the exponential term is justified. Integrating on the condition that when $y = 0$, $t = 0$,

$$y = \frac{x_o}{2} \left(\frac{kT}{-C_o e}\right) \ln \left[\left(\frac{2A}{x_o} \frac{-C_o e}{kT} \exp \frac{C_o e}{kT}\right)t + 1\right] \qquad (18)$$

which again is of logarithmic type: $y = k_o' \ln \left(\frac{t}{\tau'} + 1\right)$ where $k_o' = \frac{x_o}{2} \left(\frac{kT}{-C_o e}\right)$ and $\tau' = \frac{x_o}{2A} \left(\frac{kT}{-C_o e}\right) \exp \frac{-C_o e}{kT} = \frac{k_o'}{A} \exp \frac{-C_o e}{kT}$

We obtain, therefore, two logarithmic equations; the first, Eq. (12), expressing the thickness of oxide y as a function of time during build up of space charge having uniform charge density, and the second, Eq. (18), corresponding to build up of oxide having diffuse space charge. These two equations indicate that a change of oxidation rate should occur at the transition from the first type space charge to that of the second. Data in the literature support this conclusion, discontinuous changes in the logarithmic oxidation rate having been observed for several metals, including copper(2,3,6), iron(2,8), and zinc(7). Recent data for copper were obtained for the temperature range 150-250°C by MacNairn(57). Fig. 4 is a plot of his results at 225°C; the ~~other~~ data at other temperatures show a similar linear relation between y and log t, and an increase of the slope to a higher value at a critical thickness of oxide. Specimens of OFHC copper measuring 1 x 1 x 3/8 inch were heated in oxygen using a resistance winding cemented to one face. A thermocouple was embedded in the metal specimen, both for measuring temperature and regulating it automatically. The specimen, with surface prepared using a clean No. 4 file, was introduced into an all-glass chamber containing flowing purified N_2 and the temperature brought up to the required value using low voltage A.C. current. Oxygen was then admitted, and the time of oxidation measured from this point, after which the specimen was cooled in N_2. Thickness of the Cu_2O film was determined by cathodic reduction in 0.1 N KCl employing a small constant D.C. current.

Observed values for k_o, k_o', τ and τ' are summarized in Table II. Values of τ were obtained by extrapolating the first slope to $y = 0$, and for τ' by noting the time at which change of slope occurs. In each instance, the observed value of k_o' is consistently higher than k_o. Values of τ, inherently subject to large experimental error, vary from 0.03 to 0.3 minute averaging 0.12 minute, and for τ' vary from 6 to 14 minutes,

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(57) J. MacNairn and H. H. Uhlig, unpublished date.

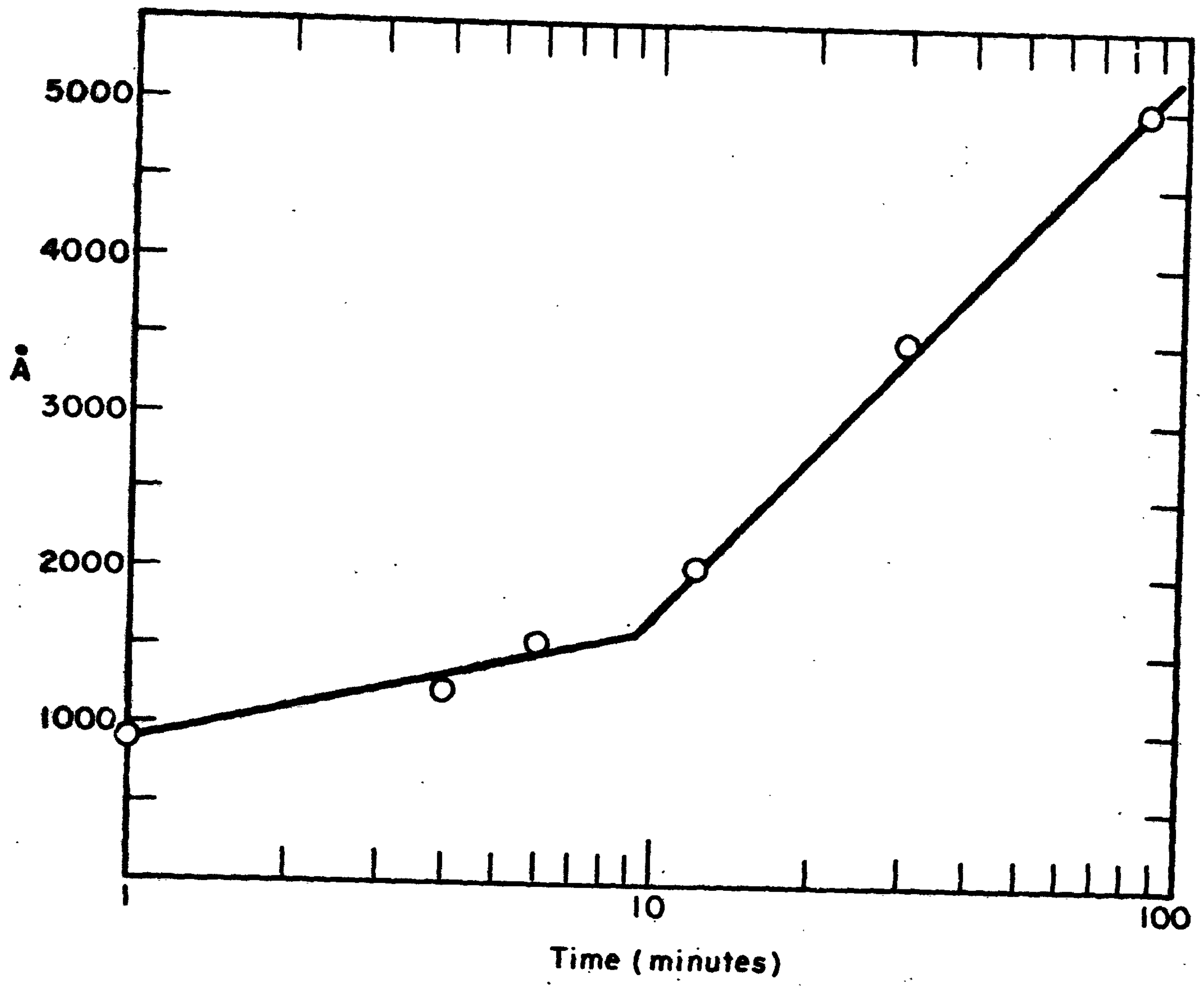

Fig. 4 Thickness of Oxide Film on Copper as a Function of Time at 225°C in Oxygen. Filed Surface.

TABLE II

OXIDATION RATE CONSTANTS FOR COPPER (MacNairn)

Temp.	k_o	k_o'	τ	τ'	L(Value of y at change of slope)
150°C	90Å	280 Å	0.3 min.	13 min.	360 Å
175°	155	520	0.1	14	750
225°	310	1630	0.06	10	1540
250°	290	2440	0.03	6	1630

averaging 11 minutes. Thickness of oxide L at which a change of slope occurs and which is equivalent, according to the foregoing theory, to thickness of that portion of the barrier layer having constant charge density, increases by a factor of 4.5 going from 150°C to 250°C. Lustman and Mehl's(3) oxidation measurements on single crystals of copper scatter appreciably, but show similarly that k_o' is consistently greater than k_o, with values generally of the same order of magnitude as data of Table II for overlapping temperatures. Their values for τ and τ' vary from 0.02 to 0.8 minute and from 8 to 80 minutes, respectively, within the temperature range 80° to 155°C. The significance of these terms will be discussed shortly.

The Cubic Equation

It is of interest to note that if the density of negative charge n in the diffuse barrier layer falls off, not as described in deriving Eq. (18), but in accord with the Boltzmann expression:

$$n = n_o \exp \frac{Ve}{kT} \qquad (19)$$

then upon substituting into the Poisson equation, the solution for potential V is of the type(58):

$$V = \frac{-2\,kT}{e} \ln \left(\frac{y}{x_o} + 1\right) \qquad (20)$$

where as before $x_o = \left(\frac{\epsilon kT}{2\pi n_o e^2}\right)^{\frac{1}{2}}$. The above solution assumes that the

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(58)Ref. 45, p. 170.

field $\frac{dV}{dy}$ tends toward zero as y approaches infinity, and V = 0 at y = 0. If instead we place the condition that at the metal surface $V = C_o$ when y = 0, where C_o is the potential at the metal surface for critical thickness of uniform barrier layer L, then

$$V = \frac{-2\,kT}{e} \ln \left(\frac{y}{x_o} + \exp \frac{-C_o e}{2kT}\right) \tag{21}$$

The sign of the potential is such that V becomes more negative the greater the oxide thickness y. Substituting into Eq. (10) for electron current from metal to oxide, which is proportional to oxidation rate, we obtain:

$$\frac{dy}{dt} = A \exp \frac{eV}{kT} \quad \text{or} \tag{22}$$

$$\frac{dy}{dt} = A \exp \ln \left(\frac{y}{x_o} + \exp \frac{-C_o e}{2kT}\right)^{-2} \tag{23}$$

Integrated on the condition that y = 0, t = 0, we obtain an equation of the cubic form:

$$\left(y + x_o \exp \frac{-C_o e}{2kT}\right)^3 = \frac{3\,A}{x_o^{2/3}}\, t + x_o^{1/3} \exp \frac{-3C_o e}{2\,kT} \tag{23a}$$

The cubic oxidation equation has been shown to hold approximately within certain ranges of temperature for oxidation of copper(24,59,60), nickel(61), titanium(62), and tantalum(62). One is led to the conclusion, therefore, that charge distribution in the barrier layer may follow more

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(59) T. Rhodin, J.A.C.S., 72, 5102 (1950).

(60) R. Tylecote, J. Inst. Metals, 81, 681 (1953).

(61) H. Engell, K. Hauffe and B. Ilschner, Zeit. Elektrochem., 58, 478 (1954).

(62) J. T. Weber, J. Chem. Physics, 20, 734 (1952).

than a single pattern, depending on experimental conditions, and that the particular pattern followed becomes apparent through the oxidation behavior of the metal.

A cubic rate equation has been derived by Mott(63,23) employing the premise that diffusion of cation vacancies is rate controlling where the number of vacancies is proportional to number of negative ions per unit surface area and to a linear field set up by the ions. Engell, Hauffe and Ilschner(61) derived a similar equation based on migration of positive holes and diffusion of lattice vancancies. The present derivation is based on electron flow from the metal as the controlling step in the oxidation process, and, hence, differs basically from both derivations of Mott, and of Engell et al. Further experimental work is needed, including effect of grain orientation, of Curie temperature and of lattice transformation on constants of the cubic equation in order to decide whether the rate for any given metal is controlled by processes of diffusion and conduction in semiconductors, or by electron flow from metal to oxide at the stage where deviations from the logarithmic equation become marked. For thicker films, where the parabolic equation takes over, it is clear through the work of Wagner(1) that ion diffusion and electric conduction processes become dominant.

Derivation of the Rideal-Jones Relation

From Eq. (11), taking the logarithm of both sides, we have:

$$\ln \frac{dy}{dt} = \frac{-e(\phi - v)}{kT} - \frac{4 \pi n e^2 \ell}{\epsilon kT} y + \ln A \qquad (24)$$

Also, from the relation $y = k_o \ln(\frac{t}{\tau} + 1)$, we have:

$$\ln \frac{dy}{dt} = \ln k_o - \ln(t + \tau) \qquad (25)$$

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(63) N. Mott, Trans. Faraday Soc., 36, 472 (1940).

Comparing (24) and (25), and remembering that $k_o = \frac{6 k T}{4 \pi n e^2 Z}$,

$$\ln k_o = \frac{-e(\phi - v)}{k T} + \ln \tau + \ln A \qquad (26)$$

The constant A is essentially temperature independent. Since $\left(\frac{dy}{dt}\right)_{t = 0} = \frac{k_o}{\tau}$, the term τ is the time necessary to oxidize the metal to thickness k_o at the initial oxidation rate. It was found by Tammann and Köster$^{(2)}$ to be strictly independent of temperature based on their oxidation data for a variety of metals. Although it is conceivable that τ may actually vary with temperature slightly for some metals and not at all for others, precision of present-day data, including values in Table II, are not adequate to imply a conclusion different from that of Tammann's. Therefore, $\frac{d \ln \tau}{d\, 1/T}$ may be considered negligible or zero and:

$$\frac{d \ln k_o}{d\, 1/T} = \frac{-e(\phi - v)}{k} = \frac{-e(\Delta E)}{k} \qquad (27)$$

where ΔE is the activation energy for oxidation in electron volts from the Arrhenius relation $k_o = \text{const} \exp \frac{-e\Delta E}{kT}$, ϕ is the work function of the metal modified by contact with the oxide, and v is a constant positive potential in the oxide at the metal surface (approximated by the electron affinity of the oxygen atom). If X_1 and X_2 are work functions of the oxide at the metal-oxide and oxide-oxygen interfaces, respectively, it follows that

$$\Delta E = \phi_o - X_1 + [X_2 - (\phi_a + \phi_e)] \qquad (28)$$

where ϕ_o is the work function of the metal, ϕ_e is the electron affinity of oxygen and ϕ_a is a small additive energy introduced by adsorption of oxygen on the oxide. If $X_1 = X_2$,

$$\Delta E = \phi_o - (\phi_a + \phi_e) = \phi_o - K \qquad (29)$$

which is the Rideal-Jones relation as applied to oxidation of metals forming thin, non-volatile oxides, and is the empirical expression originally proposed for W, Pt and C which form volatile oxides.

If the work function of the oxide at the metal interface X_1 is less than the work function X_2 at the oxygen interface, then K will be larger than the value calculated from Eq. (29) above. This may be the situation for both Cu and Fe. Values of $\phi_o - \Delta E$ or of K for Cu are $4.5 - 0.28 = 4.3$ e.v., and for Fe are $4.4 - 0.30 = 4.1$ e.v., where the activation energy for Cu is taken from MacNairn's data, and for iron from Davies, Evans and Agar's(11) data*. The work functions are from Michaelson(38). These values of K are larger than 3.6 e.v., the average value for elements listed in Table II. When more precise data are available both for metal work functions and for activation energies of oxidation, more definite conclusions will be possible than are now warranted.

Using a derivation similar to that given above, it can also be shown that

$$\frac{d \ln k_o'}{d\, 1/T} = \frac{C_o e}{k} \qquad (30)$$

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*Since the logarithmic equation applies to the oxidation of iron over the temperature range considered, the activation energy is obtained from the slope of log weight gain at t = constant vs $\frac{1}{T}$. This follows from the proportionality between thickness of oxide y and weight gain, and the fact that $\ln y = \ln k_o + \ln \ln (\frac{t}{\tau} + 1)$. Hence, since τ is a constant and t is held constant, $\frac{d \ln y}{d \frac{1}{T}} = \frac{d \ln k_o}{d \frac{1}{T}} = \frac{-e\Delta E}{k}$ where k is Boltzmann's constant. Data in Fig. 13 of Davies, Evans and Agar's paper(11) show that essentially the same activation energy is calculated for various times of oxidation (15 minutes to 8 hours) in the logarithmic range, with the exception of the 15- and 30-minutes runs where experimental error is perhaps greatest.

where C_o is given by Eq. (16), and k_o' is the second and steeper slope obtained by plotting y vs ℓn t.

DISCUSSION

In accord with Equations (27) and (30), plots of log k_o and log k_o', using data of Table II, vs $\frac{1}{T}$ provide means for calculating (ϕ - v) and $-C_o$, respectively. From slopes of data so plotted in Fig. 5, these values are 0.28 e.v. and 0.42 e.v., respectively. Since $C_o = \frac{-4\pi n e \ell L}{\epsilon} - (\phi - v)$ (Eq. 16), we know all terms of this equation except the product $n\,\ell$, for which we can solve. On the basis that $\epsilon = 10.5$ and observed L at 225°C = 1540 Å (Table II), $n\,\ell = 5.3 \times 10^{10}$. Also, from the relation $k_o = \frac{\epsilon k T}{4\pi n e^2 \ell}$ and employing the observed value for k_o at 225°C equal to 310 Å, we obtain $n\,\ell = 8.1 \times 10^{10}$ which is in reasonable agreement with the value calculated from C_o and (ϕ - v). We can next calculate a value for n_o from the relation given in Eq. (18) that $k_o' = \frac{x_o}{2}\left(\frac{kT}{-C_o e}\right)$, and from the observed value of k_o' = 1630 Å, where $x_o = \left(\frac{\epsilon k T}{2\pi n_o e^2}\right)^{\frac{1}{2}}$. The corresponding value for n_o is 4.9×10^{12}, which is the density of available sites for trapped electric charge in the diffuse space charge layer. This density is equivalent to about one lattice site for every 5×10^9 molecules of Cu_2O.

We have next to check how density n_o compares with density n of trapped electrons in the uniform space charge layer. Since only the product $n\,\ell$ is known from experiment, an estimate of ℓ must be made through Eq. (7) substituting $V = -\phi$ at $y = \ell$ and $C_2 = -(\phi - v)$. It follows that $v = \frac{4\pi n e \ell^2}{2\epsilon}$. Since the value of v is the same order as K (Eq. 29) or the same order as the modified electron affinity of oxygen equal to 3.6 electron

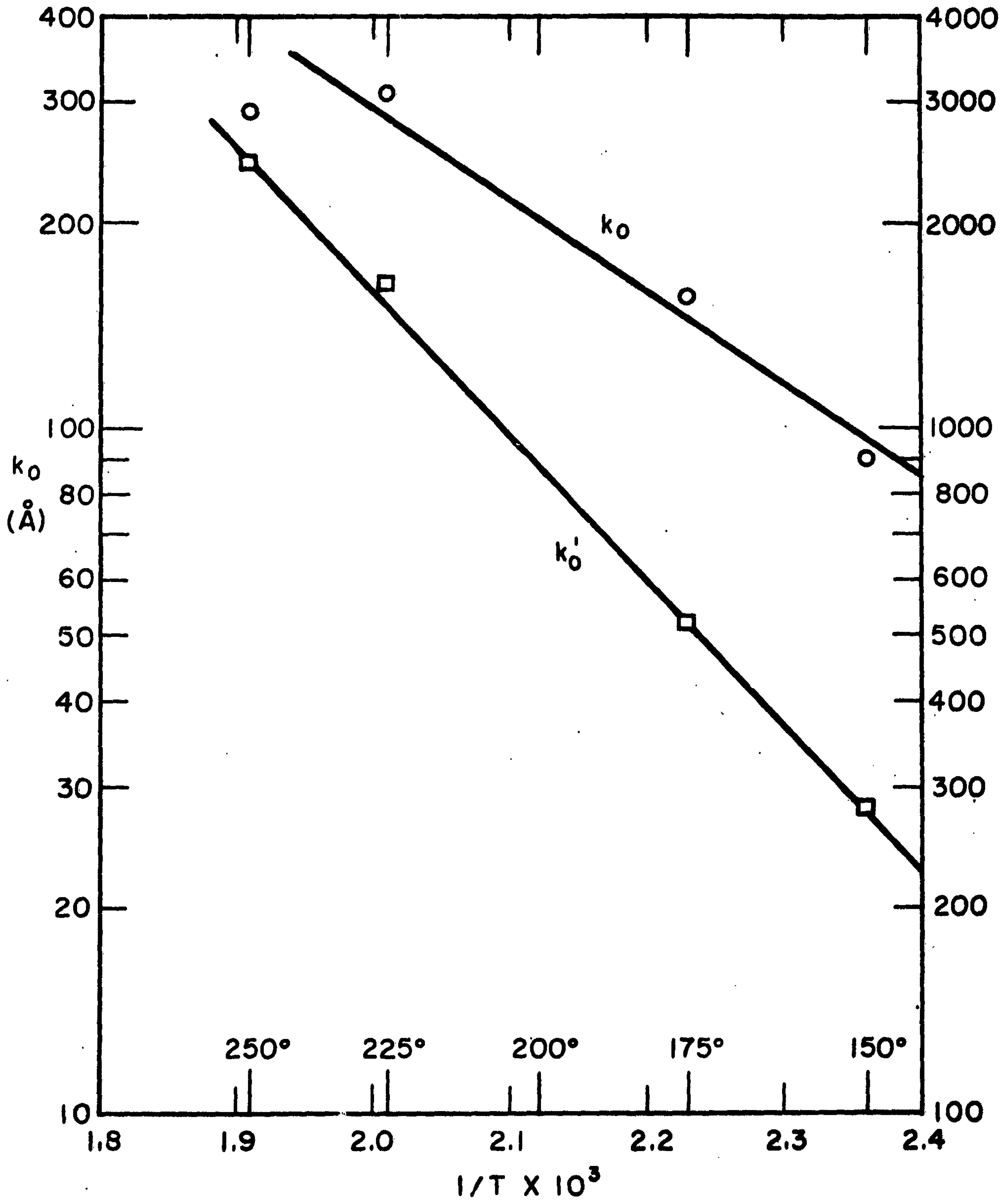

Fig. 5 Plots of k_o and k_o' vs Reciprocal Absolute Temperature for Copper Oxidized in Oxygen. Filed Surfaces.

volts, we find substituting 6.7×10^{10} for the average value of $n\ell$, in accord with the foregoing calculations, that $\ell = 6.2 \times 10^{-4}$ cm. This value for ℓ represents the theoretical maximum thickness of the uniform charge density barrier layer (the diffuse barrier layer may be considerably thicker). It is larger than the observed thickness of uniform barrier layer L by a factor of about 40, and should be approximately comparable with the thickness of the "blocking" layer next to the copper surface in the Cu-Cu_2O rectifier. The thickness of the blocking layer is estimated from capacitance measurements to be about 10^{-4} cm(64), which is not far from the above calculated value for ℓ.

Knowing the value for ℓ, the value for n, therefore, equals $\frac{6.7 \times 10^{10}}{6.2 \times 10^{-4}}$ or 1.08×10^{14}. Accordingly, the actual density of trapped charge in the Cu_2O layer of thickness L next to the metal appears to be larger than the density (4.9×10^{12}) of available sites for trapped charge in the diffuse space charge layer farther away from the metal surface.

This relative difference in density persists, although absolute densities increase, if correction is made for the larger absolute surface compared to the geometrical surface of a filed copper surface. Assuming a roughness factor of 3, comparable with published values of 3.8(65) and 2.5(66) for abraded metal surfaces, film thickness values such as those

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(64) Ref. 45, page 178.

(65) R. Powers and N. Hackerman, J. Electrochem. Soc., 100, 314 (1953).

(66) O. Erbacher, Zeit. Physik. Chem., 163, 215 (1933); Chemiker Zeit., 62, 601 (1938).

in Fig. 4. would be decreased to 1/3 the given values, and both n_o and n would increase by a factor of 9, making the densities approximately 5 x 10^{13} and 10^{15}, respectively. Values of ℓ and L correspondingly would be reduced by 1/3.

Values for n, ℓ, and n_o calculated from MacNairn's data at several temperatures and not corrected for roughness factor are given in Table III. Values of $n\ell$ are averages of values obtained from observed k_o and L, with the exception of 250°C where only the value obtained from L was used. This procedure was followed because the value for k_o at 250°C falls off the line in Fig. 5. If the value for k_o were included, the corresponding calculated value for $n\ell$ is 0.9 x 10^{11} compared with 0.5 x 10^{11} given in Table III. It is evident that for cuprous oxide in contact with copper, n_o decreases with temperature (fewer sites for trapped charge in the diffuse barrier layer as the temperature increases). This is also true of n, the actual charge density in the uniform space charge layer. Accordingly, the equilibrium:

$$\text{Bound hole + free electron} \leftrightarrows \text{trapped electron}$$

is displaced to the left as the temperature increases. The observed increase of ℓ with temperature parallels extension of the space charge to greater distances into the oxide the higher the temperature. This trend is also reflected by increased observed thickness L for the uniform barrier layer (Table II).

Brattain(67) calculated the density of holes in Cu_2O as function of temperature from conductivity of the oxide and mobility of carriers. He found that a limiting upper density, equal to the density of electron

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(67) W. Brattain, Rev. Modern Physics, 23, 203 (1951).

TABLE III

NUMERICAL EVALUATION OF TERMS IN LOGARITHMIC OXIDATION RATE EQUATIONS

Temperature	$n \ell$ (cm)$^{-2}$	n_o	n	ℓ (cm)
150°C	2.3×10^{11}	1.0×10^{14}	1.3×10^{15}	1.8×10^{-4}
175°C	1.3×10^{11}	3.5×10^{13}	3.8×10^{14}	3.3×10^{-4}
225°C	0.67×10^{11}	4.9×10^{12}	1.1×10^{14}	6.2×10^{-4}
250°C	0.50×10^{11}	2.6×10^{12}	0.60×10^{14}	8.4×10^{-4}

acceptors minus density of acceptors occupied by electrons from higher lying donor levels, occurs in the range 100°C or higher and that the limiting density is 10^{15} for OFHC copper and 10^{14} for Chile copper. These values are reasonably comparable with the calculated density of charge n or density of defect sites for bound electrons n_o in Table III. His calculations, however, show that the density of holes does not decrease with temperature, but instead is relatively insensitive to temperature in the region of 100°C or higher, and that below 100°C the density increases with temperature.

The value for A in Eq. (11) can be calculated from the relation following Eq. (13), $\tau = \frac{k_o}{A} \exp \frac{e(\phi - v)}{kT}$. At 225°C, for example, $\tau = 3.6$ seconds, $k_o = 310$ Å, $(\phi - v) = 0.28$ volt. Therefore, $A = (0.86 \times 10^{-6}) e^{6.53} = 5.9 \times 10^{-4}$ cm/sec. It will be remembered that $A = A'\beta$ where β expresses the relation between electric current and rate of oxide growth, and whose value for density of $Cu_2O = 6$, is 1.23×10^{-4} cm³/coulomb. The value for A' in Eq. (10), accordingly, equals $\frac{5.9 \times 10^{-4}}{1.23 \times 10^{-4}} = 4.8$ amp./cm². The average value for A' for all temperatures of Table II is 2.2 amp./cm². Similarly, the average value of A' from the relation $\tau' = \frac{k_o'}{A} \exp \frac{-C_o e}{kT}$ averaging all values of τ' and $k_o' \exp \frac{-C_o e}{kT}$ is equal to 3.5 amp./cm². These two values are the same order of magnitude. These average values of A', if corrected for a roughness factor of 3, would be 1/3 the given values.

The ratio $\frac{\tau'}{\tau}$ as derived from Eq. (12) and (18) is equal to the expression $\frac{k_o'}{k_o} \exp(-C_o e/kT - e(\phi - v)/kT)$. The exponential factor is a constant at any given temperature since $-C_o$ and $(\phi - v)$ are constants equal to 0.42 and 0.28 volt, respectively. At 225°C, for example, $\frac{\tau'}{\tau} =$

$\frac{1630}{310}$ exp 3.3 = 143. The observed ratio is $\frac{10.0}{0.06}$ = 167 which is of the same order of magnitude . The average of calculated ratios for $\frac{\tau'}{\tau}$ for all temperatures is 153 corresponding to an observed average (Table II) of 138 showing that the agreement of theory with experiment is good.

The described dependence of oxidation rate on work function of the metal and on properties of semi-conducting oxides in contact, immediately suggest several reasons for experimental hurdles usually encountered in reproducing thin-film oxidation behavior. Despite refined techniques for metal surface preparation and gas purification, it is extremely difficult to avoid the trace impurities which greatly affect the metal work function, and also the number of sites available for trapped charge in oxide films. The major influence of trace impurities in semi-conducting germanium and silicon has only recently been fully appreciated in connection with the use of these substances for rectifiers and for transistors. Added to the marked effect of impurities, often present in amounts below common analytical techniques, is the appreciable effect of thermal treatment on the density of lattice imperfections in semi-conductors. It is little wonder that various investigators have reported difficulty in reproducing oxidation data at low temperatures; Vernon, Akeroyd and Stroud(7) reported such difficulties in their study of zinc, Leontis and Rhines(47) in their study of magnesium and Brasunas and Uhlig(29) in their studies of Cr-Fe alloys. A full appreciation of the various factors entering thin film oxidation should help such studies in the future.

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