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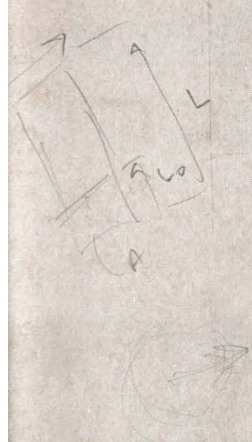
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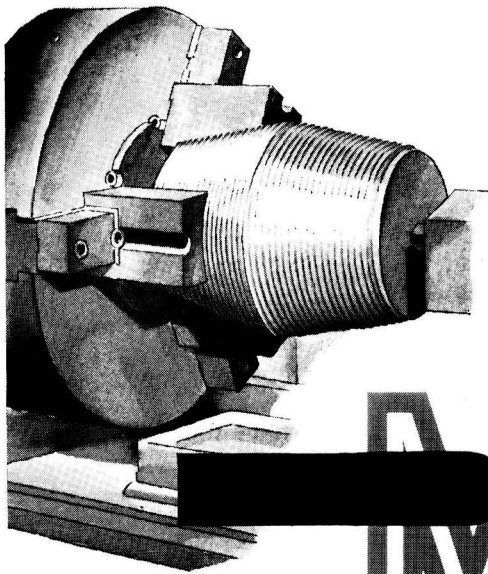
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87C

FUTURE MEETINGS OF The Electrochemical Society



San Francisco, April 29, 30, May 1, 2, and 3, 1956

Headquarters at the Mark-Hopkins Hotel

Sessions will be scheduled on

Corrosion (joint symposium with Theoretical),
Electric Insulation, Electronics (including Luminescence and Semiconductors),
Electrothermics and Metallurgy, Industrial Electrolytics,
and Theoretical Electrochemistry

★ ★ ★

Cleveland, September 30, October 1, 2, 3, and 4, 1956

Headquarters at the Statler Hotel

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Batteries, Corrosion, Electrodeposition,
Electrothermics and Metallurgy, and Theoretical
Electrochemistry (joint with Electrodeposition)

★ ★ ★

Washington, D. C., May 12, 13, 14, 15, and 16, 1957

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New York, April 27, 28, 29, 30, and May 1, 1958

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Ottawa, September 28, 29, 30, October 1, and 2, 1958

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Papers are now being solicited for the meeting to be held in Cleveland. Triplicate copies of each abstract (*not exceeding 75 words in length*) are due at the Secretary's office, 216 West 102nd Street, New York 25, N. Y., *not later than June 15, 1956* in order to be included in the program. *Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

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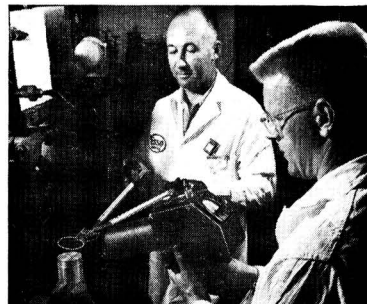
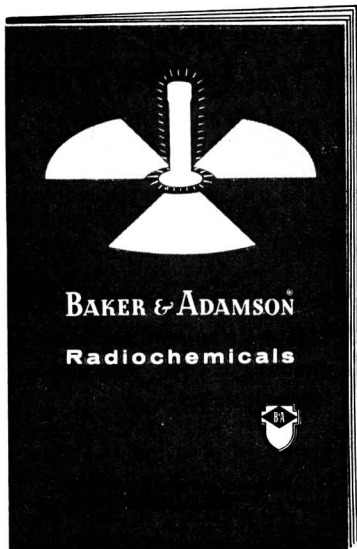
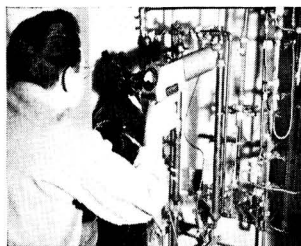


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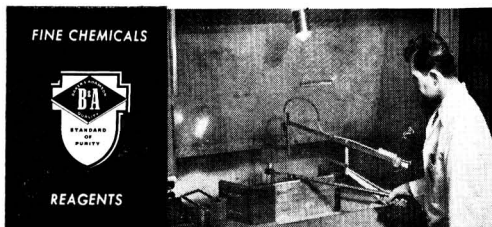
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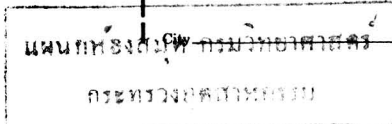
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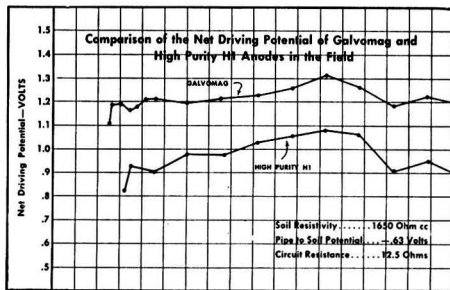
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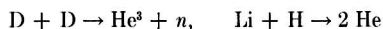


Energy from Nuclear Fusion

SINCE THE FIRST H-bomb explosion in 1952, it has been evident that thermonuclear reactions of light elements might some day be controlled to provide an enormous new source of peacetime energy. At the Geneva "Atoms-for-Peace" Conference in August 1955, Dr. Homi Bhabha pointed out that conversion of the deuterium in the oceans into helium could provide ten million times as much energy as all the fossil fuels, uranium, and thorium on the earth. Several other light element reactions may be equally feasible. Direct conversion of ordinary hydrogen to helium is ruled out, but some of the intermediate steps might be practical.

The Conference also revealed that several nations are actively working on the problems of controlling such reactions. The U. S. Atomic Energy Commission has studies under way at five centers, and has made it plain that money will be available for research and development as working ideas are found. Against much scientific and Congressional protest, the Commission has thus far insisted that the magnitude of the effort and the nature of the studies must remain secret. This is justified only insofar as it protects details of the H-bomb, and is unfortunate in that only a few people can contribute with ideas, speculation, or experiment.

Reactions of light element nuclei, such as

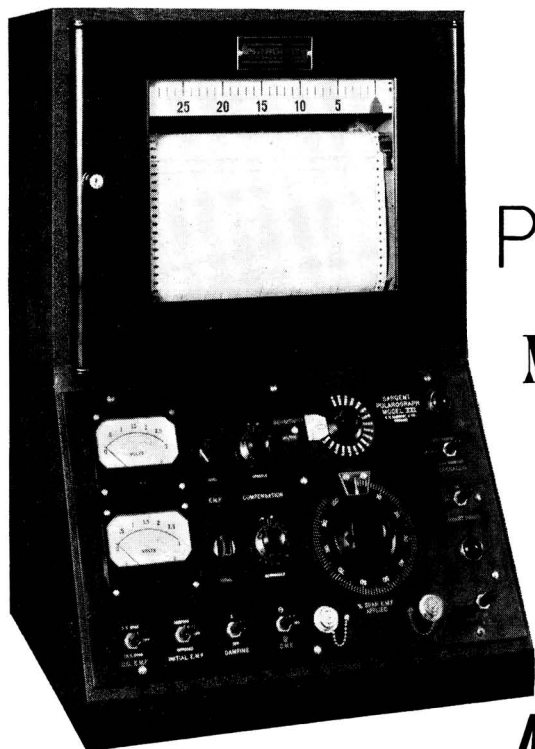


have long been known from ion-accelerator experiments. They take place with loss of mass and release of energy amounting to several million electron-volts, more than 10^{11} cal for gram-atom quantities. Collision frequencies and activation energies can be estimated well enough to predict useful rates at temperatures of 10^7 to 10^9 degrees. The calculations were confirmed by the H-bomb.

On the earth such temperatures have been reached, on a significant scale, only in atom bomb explosions, and it does not seem practical to "light the furnace" with an atom bomb. On the other hand, the atomic velocities equivalent to these high temperatures are only about 1% of the speed of light, and are readily attainable in conventional ion-accelerators. A large power plant by today's standards would need to "burn" only a few hundred grams of atomic fuel per day if the reaction were at all efficient. Ion beam currents approaching 1 amp, corresponding to 1.5 g of accelerated deuterium atoms per day, have been found possible; unfortunately only 1 ion in 10^6 or 10^7 causes reaction in the usual targets. Perhaps eventually it will be possible to nourish a partly self-sustaining short chain reaction with a beam of hot ions. Since no materials of construction can withstand such temperatures, it will be necessary to maintain a suitable temperature gradient to the furnace walls, as with a spread-out ion beam impinging on a solid target which slowly vaporizes away.

In the 1930's we read in the science fiction magazines about space ships powered by cyclotrons (eyes-for-short), pushing the "Einstein barrier" in speed. Not quite so fantastic now as then.

—CVK



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The Kinetics of the Corrosion of Copper in Acid Solutions

JOHN RANDEL WEEKS¹ AND GEORGE RICHARD HILL

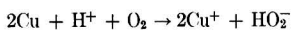
Institute for the Study of Rate Processes, Metallurgy and Fuel Technology Departments, University of Utah, Salt Lake City, Utah

ABSTRACT

The mechanism of the initial corrosion of copper in hydrochloric acid solutions has been investigated, using a radioactive tracer technique. Kinetic data have been obtained showing the effect of pH, dissolved oxygen, chloride ion, and temperature on the corrosion rate. Surface areas were measured using a modified electrolytic method. On the basis of these data (reproducible to $\pm 20\%$), a mechanism for the initial corrosion process is proposed and discussed. Specific rate constants, heats, and entropies of activation for the slow step in the corrosion process were determined.

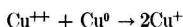
INTRODUCTION

The initial rate of corrosion of copper by neutral chloride solutions has been determined recently (1). Under conditions where the chemical reaction at the metal surface itself is the rate-determining factor, a corrosion rate corresponding to 1600 mdd was measured in a neutral, normal potassium chloride solution. From kinetic data obtained by experimental measurement of the amount of electricity necessary to electroreduce the cuprous oxide produced by the initial reaction, the following rate-determining step of the initial process was proposed:



In acid chloride solutions in which the Cu_2O produced is soluble, the earlier experimental method is no longer applicable. The initial corrosion mechanism might, however, be expected to proceed for some time in these solutions, provided diffusion of the reacting species to the metal surface does not become rate-determining. The purpose of the present investigation was to examine the kinetics of the initial reaction of copper with acid chloride solutions in order to investigate the corrosion mechanism.

The dissolution of copper in hydrochloric acid over extended periods of time has been investigated recently by Katz (2, 3). He reported that the corrosion rate gradually increases over periods of several days, and postulated that the cupric ions that build up in the solution accelerate corrosion by reacting according to the equation,



Such a reaction, however, clearly cannot represent an initial corrosion process.

Recent polarographic investigations by Delahay (4, 5) on the reduction of oxygen on various metals indicated that in many cases hydrogen peroxide is produced as an intermediate product in solution corrosion processes. Possible subsequent reactions of this hydrogen peroxide have been considered by van Rysselberghe and co-workers

¹ Present address: Brookhaven National Laboratory, Upton, N. Y.

(6-8) to play an important role in the understanding of corrosion behavior.

EXPERIMENTAL

Corrosion rates were measured by a radioactive tracer method. Because there are no suitable isotopes of copper, the pure metal, to which approximately 0.01% radioactive cobalt had been added, was used in this investigation. In addition to its availability, long half-life, and high specific activity, cobalt 60 was selected because it is considerably electropositive with respect to copper and forms a solid solution alloy with it to a sufficient extent. A homogeneous alloy of this type would be expected to corrode at approximately the same rate as pure copper; as the cobalt atoms appear on the metal surface, they, being electropositive to the copper atoms, should dissolve preferentially by a simple galvanic mechanism. The rate of appearance of activity in the solution would therefore indicate the rate of corrosion of the copper.

Samples were prepared by electroplating approximately 0.001 g of radioactive cobalt on a small strip of pure copper. This coated strip, with sufficient additional copper to bring the total sample weight to 10 g, was vacuum sealed in a short length of $\frac{1}{4}$ in. fused silica tubing. The sample was melted and held in the liquid state for one hour, after which it was quenched in an oil bath. Preliminary investigations using nonradioactive cobalt showed that this treatment produced a uniform, fine-grained alloy in samples containing 0.10% cobalt in copper. The sample thus produced was roughly cylindrical with tapered ends and showed several surface pit-like indentations. No internal porosity was noted in six samples.

All corrosion rates were measured from the same sample, which was stored in a small glass vial of acetone between experiments. All water used in the experiments was redistilled from an alkaline solution of potassium permanganate into a Yycor condenser. Fresh corrosion solutions were made frequently using this purified water. All glassware was cleaned in dichromic acid, and rinsed thoroughly with tap, distilled, and redistilled water. Extreme laboratory cleanliness was found necessary to obtain reproducible results. Reproducibility also re-

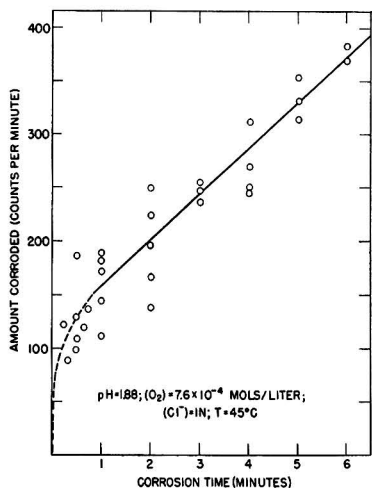


Fig. 1. Effect of time on the corrosion of copper in acid chloride solution.

quired that a series of experiments using a given corrosion solution be performed within 24 hr after the solution was made.

At the beginning of an experiment, the sample was transferred directly from the glass vial into a Pyrex holder, rinsed in fresh acetone, and cleaned 1 min in a 10% solution of ammonium persulfate. This treatment was known from previous experience (1) to yield a clean, oxide-free surface. The cleaned sample was transferred quickly into two successive beakers of re-distilled water, and then placed in the beaker of corrosion solution. After a measured corrosion time, the sample was removed from the solution, rinsed, and returned to a vial of fresh acetone until again needed. Thirty-five ml of corrosion solution was placed in a 50 ml beaker for each experiment. The beaker was suspended 30 min in a constant temperature water bath before the corrosion sample was admitted. Solutions were covered and stirred by passing a stream of gas of known composition through a sintered glass orifice immersed into them through a hole in the cover glass. After the metal sample was removed, the cover glass and gas orifice were rinsed into the sample solution. The solution was then diluted to bring its level to a known height in the beaker, and was placed directly beneath the end-window of a G-M counting tube. Thus, all samples were counted under as nearly identical geometry as practicable. Conversions to absolute units were made by measuring the sample weight loss in 15 and 30 min attack by the persulfate cleaning solution, and measuring the activity of the resultant solution as before. The corrosion rate in mdd was found to be equal to the measured rate in counts per minute for 10-min corrosion time multiplied by 44.7 and divided by the surface roughness factor.

The surface area of a similar, nonradioactive sample was estimated using a modified Bowden-Rideal electrolytic method (9). The charge placed on the metal surface during a known increment of its cathodic polar-

ization in a dilute acid solution was recorded using a calibrated electrolytic capacitor placed in series with the metal-solution interface. By comparing the amount of this charge with that measured on a mercury surface of known area, the surface area of the unknown sample could be calculated. This method (10) is somewhat similar to that proposed by Wagner (11). The surface area of the sample as cast was approximately 80 times the apparent area. After being treated by three cleaning-corroding cycles like the one discussed, the true area had decreased to 35 times the apparent area. This roughness factor decreased steadily to a value of 9.2 after prolonged etching in ammonium persulfate (equivalent to the dissolution effect of nearly 100 cycles). After 6 hr in the etching solution, the roughness factor was still nearly five. Nearly 60 corrosion cycles were performed before reproducible data were obtained. At this time, the surface roughness factor was probably nearly 20; it dropped gradually to a value of about 5 after 300 samples had been run. A surface area change of this magnitude was found to agree with the corrosion rate data.

RESULTS

The rate of corrosion of copper in dilute hydrochloric acid solutions was measured as a function of time, pH, concentration of dissolved oxygen, and temperature, in order to determine the corrosion mechanism. All solutions were maintained 1*N* in chloride ion concentration by mixing HCl and KCl to give a solution of the desired acidity. All rate data, except for the temperature effect measurements, were obtained at 45°C in order for the rate to be large enough for convenient measurement. All solutions, except those for determining the oxygen concentration effect, were stirred with a stream of oxygen. All solutions were of pH range 0.8 to 2.8; in this range of acidity no evidence of surface oxide was noted even after extended corrosion times. Because of an appreciable scatter in experimental data, measurements had to be repeated several times in order to evaluate the results obtained. This scatter can perhaps be attributed to possible segregation of the cobalt tracer atoms in the alloy, oxide inclusions in the alloy, and fluctuations in the surface area of the sample during cleaning. With sufficient data, however, mean average rates were definite, reproducible, and probably accurate within $\pm 20\%$.

Effect of Time: After a rapid corrosion during the first few seconds, the amount of corrosion products obtained varied linearly with time, as seen in Fig. 1. This linear relationship continued at least to 40 min corrosion time. The reaction rate, or slope of the linear portion of the curve, is 400 counts per minute per 10 min corrosion time. Assuming the surface roughness factor on these first experiments to be 20, this value corresponds to 90 mdd. The intercept obtained from extrapolating time curves to zero time proved to be nearly independent of the variables investigated, except the surface area; it thus served as a useful indication of the change of surface roughness of the sample. The interpretation given the very rapid initial corrosion rate will be discussed later.

Effect of pH: The variation of the corrosion rate with pH is shown in Fig. 2. The rate of dependence on the

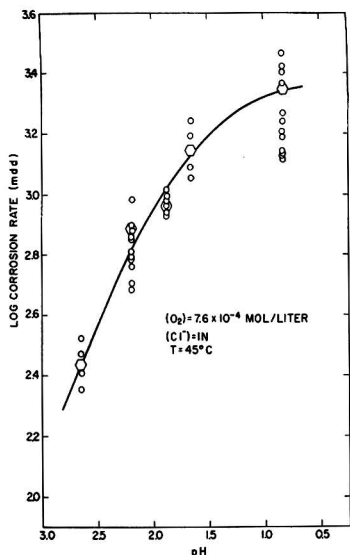


FIG. 2. Effect of pH on the corrosion rate

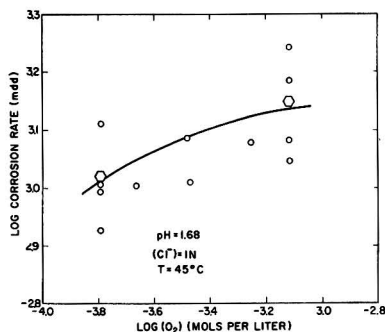


FIG. 3. Effect of dissolved oxygen concentration on the corrosion rate.

acid concentration is seen to be somewhat less than first order, and to decrease with increasing acidity. In this figure, the measured rates have been converted to mdd. The smooth curve is a plot of the rate equation derived in the next section. Other results, using very acid solutions, under somewhat different conditions, indicated that there is very little increase in corrosion rate due to increasing the acidity above 0.1*N*. Low corrosion rates in solutions less acid than 0.001*N* made reproducible data difficult to obtain by the method used.

Effect of Oxygen Concentration: A typical variation of the corrosion rate with oxygen concentration is shown in Fig. 3. Here again the smooth curve is that of the rate equation derived in the next section. Oxygen, compressed air, and known mixtures of oxygen and nitrogen were used to stir the solutions. The concentration of dissolved oxygen in the solution was considered from Henry's law to be equal to the fractional pressure of oxygen in the gas mixture times the solubility of pure oxygen in water at

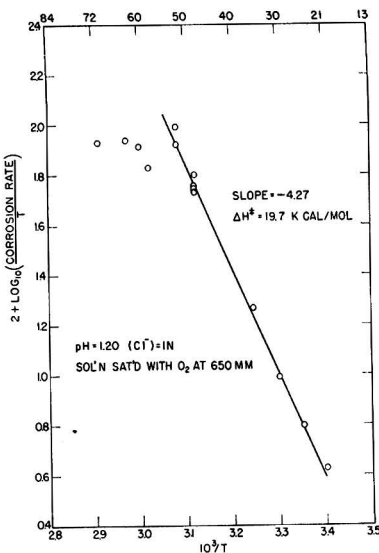


FIG. 4. Effect of temperature on the corrosion rate

the prevailing conditions of temperature and pressure. The solution was assumed to have been aspirated at a sufficient rate to maintain oxygen saturation. Many similar curves were obtained, each using a solution of slightly different pH. The rate dependence on oxygen concentration is seen to be somewhat less than half-order; with increasing acidity this dependence decreases. Many curves at a pH of 0.8 to 1.0 showed little distinguishable effect of oxygen pressure.

Effect of Stirring Rate: No appreciable effect on the corrosion rate was observed when the rate of aspirating the solution was either increased or decreased by a factor of five from the rate normally used in these experiments. This suggests that transfer of reactants to the metal surface is not controlling the process.

Effect of Temperature: The corrosion rate was measured over a temperature range from 20° to 70°C. In Fig. 4, the data obtained are plotted as log rate/*T* vs. 1/*T*, according to the theory of absolute reaction rates:

$$\text{Rate} = C \frac{kT}{h} e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}}$$

when the reactants are in constant concentration. At temperatures from 21° to 52°C, the measured rates are seen to lie on a straight line, when corrected for variations in oxygen solubility, assuming $\frac{1}{2}$ order dependence (these corrections were quite small). From the slope of this line, the heat of activation, ΔH^\ddagger , for the reaction was found to be 19.7 kcal/mole. This value clearly indicates that the rate of the process studied was controlled by chemical reaction rather than by diffusion of the reactants, according to King's criteria (12). The marked decrease in the temperature coefficient above 52°C was possibly due to a shift in the control of the reaction rate to diffusion of dissolved oxygen to the metal surface. This shift is thought to be due to a combination of the

TABLE I. Corrosion in the "absence" of oxygen

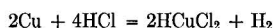
Solution	Measured rate c/m/10 min corrosion
HClO ₄ + KClO ₄ (Sat)	72
HClO ₄ + KClO ₄ (Sat)	74
HCl + KCl (1 <i>N</i>)	66
HCl + KCl (1 <i>N</i>)	75

$pH = 0.96$, $T = 45.5^\circ\text{C}$, solution aspirated with pure nitrogen.

decreasing solubility of oxygen and the rapidly increasing reaction rate at these high temperatures. Other data obtained in the higher temperature region at a slightly different pH show an activation energy of about 5 kcal/mole and a temperature rate coefficient of 1.3; these values comply with King's criteria for diffusion-controlled reaction (12).

The shift in mechanism was never found to occur at a temperature lower than 52°C in four experiments using solutions of different pH . Thus, it is felt that the temperature selected for the investigation of concentration effects, 45°C , was within the range of chemical rather than diffusion control.

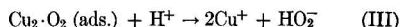
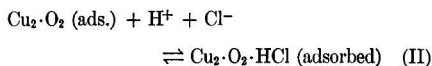
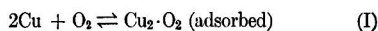
Corrosion in the Absence of Oxygen. Copper has been reported (13) to be attacked by HCl in the absence of oxygen according to the reaction,



Since it was not possible to exclude oxygen entirely from the solution with the apparatus used, the effect of this reaction was investigated indirectly by comparing the rates of solution of copper in hydrochloric and perchloric acid solutions of the same pH which were stirred with a stream of nitrogen. The measured rates from the two solutions were identical within the limits of experimental error, as seen in Table I. Therefore, it was considered that the amount of copper dissolved according to the above equation was negligible under the conditions of the experiments.

MECHANISM OF THE REACTION

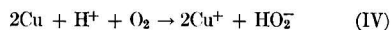
In order to explain the measured dependence of the corrosion rate on the reactants investigated, the following sequence of reactions is proposed:



The first stage of oxidation is the reversible adsorption of a dissolved oxygen molecule from the solution on a pair of copper atoms on the metal surface, forming an "oxidized site." This is followed either by adsorption of H^+ and Cl^- ions in pairs² from the solution on the oxidized site, as shown by equation (II), or by discharge of the oxidized site due to collision with a hydrogen ion from the solution, as shown by equation (III). The net reac-

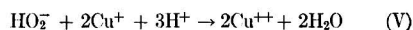
² Or a neutral HCl molecule.

tion for this rate-determining portion of the reaction sequence is

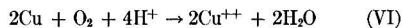


which is identical with that proposed by Hill (1) for the slow step in copper corrosion in neutral or basic solutions, and is similar to that discussed by Delahay, Pourbaix, and van Rysseberghe (14) for the first stage of the anodic reduction of oxygen. The concept of adsorption of oxygen as (O_2^-) in the initial stage of anodic reduction, followed by production of (HO_2^-) by reaction with hydrogen ions is due in part to Berl (15), who also established that the biperioxide ion is frequently an intermediate product in the reaction mechanism.

Before examining the above reactions in terms of the experimental data, first consider possible subsequent reactions in the solution phase. Experimentally, the copper was found in solution as Cu^{++} ; tests for hydrogen peroxide in the bulk solution were negative. Copper ions have been observed to decompose H_2O_2 catalytically (16). The mechanism for this type of decomposition was first discussed by Haber and Wilstatter (17), Haber and Weiss (18), and more recently by Evans, Baxendale, and Park (19). A catalytic decomposition similar to that described by these last authors predicts a net reaction for the solution phase of



The net reaction for the over-all corrosion process then becomes



Derivation of the rate equation.—Since it was the rate at which the copper atoms leave the metal surface that was measured experimentally, an expression for the reaction rate derived from a steady-state consideration of reactions (I), (II), and (III) must satisfy the experimental data. Letting x represent the fraction of the metal surface covered with "oxidized sites," y the fraction of the surface taken up by "oxidized sites" upon which acid adsorption has taken place, and s the fraction of unoccupied sites on the metal surface, the steady-state equations for the reaction sequence become

$$\frac{dx}{dt} = 0 = \bar{k}_1 s (\text{O}_2) - \bar{k}_1 x \quad (\text{VII})$$

$$- \bar{k}_2 x (\text{H}^+) (\text{Cl}^-) + \bar{k}_2 y - \bar{k}_3 x (\text{H}^+)$$

$$\frac{dy}{dt} = 0 = \bar{k}_2 x (\text{H}^+) (\text{Cl}^-) - \bar{k}_2 y \quad (\text{VIII})$$

$$s + x + y = 1 \quad (\text{IX})$$

where \bar{k}_1 and \bar{k}_1 are the specific reaction rate constants for the adsorption and desorption, respectively, of oxygen on the metal surface (I); \bar{k}_2 and \bar{k}_2 are the specific reaction rate constants for the adsorption and desorption, respectively, of HCl on the "oxidized sites" (II); and \bar{k}_3 is the specific reaction rate constant for reaction (III).

From these equations can be readily derived the useful relationships

$$x = \frac{\bar{k}_1 s(\text{O}_2)}{\bar{k}_1 + k_3(\text{H}^+)} = \frac{K_1 s(\text{O}_2)}{1 + (k_3/\bar{k}_1)(\text{H}^+)} \quad (\text{X})$$

where

$$K_1 = \frac{\bar{k}_1}{\bar{k}_1} \quad (\text{Xa})$$

$$y = \frac{\bar{k}_2 x(\text{H}^+)(\text{Cl}^-)}{\bar{k}_2} = K_2 x(\text{H}^+)(\text{Cl}^-) \quad (\text{XI})$$

where

$$K_2 = \frac{\bar{k}_2}{\bar{k}_2} \quad (\text{XIa})$$

and

$$s = \frac{1 + (k_3/\bar{k}_1)(\text{H}^+)}{1 + (k_3/\bar{k}_1)(\text{H}^+) + K_1(\text{O}_2)\{1 + K_2(\text{H}^+)(\text{Cl}^-)\}} \quad (\text{XII})$$

The rate of appearance of copper ions in solution from reaction (III) is

$$\frac{d(\text{Cu}^+)}{dt} = k_3 x(\text{H}^+) \quad (\text{XIII})$$

Combining (XIII) with (X) and (XII), one has an expression for the reaction rate:

$$\frac{d(\text{Cu}^+)}{dt} = \frac{k_3 K_1 (\text{H}^+) (\text{O}_2)}{1 + (k_3/\bar{k}_1)(\text{H}^+) + K_1 (\text{O}_2) \{1 + K_2 (\text{H}^+) (\text{Cl}^-)\}} \quad (\text{XIV})$$

Evaluation of constants—The constants appearing in the rate expression (XIV) were evaluated from the reaction rate dependence on the hydrogen ion and oxygen concentrations. The average experimental data used, shown by hexagons in Fig. 2 and 3, are given in Table II. These were substituted into equation (XIV), and numerical values of the constants obtained by solving simultaneously all combinations of five of the seven resultant equations. Average values obtained were (at 45°C)

$$k_3 = 1.51 \times 10^5 \text{ (mdd)(1/mole)}$$

$$k_1 = 1.64 \times 10^4 \text{ 1/mole}$$

$$k_2 = 54.9 \text{ 1/mole}$$

$$\bar{k}_1 = 3.28 \times 10^7 \text{ (mdd)(1/mole)}$$

$$\bar{k}_1 = 2 \times 10^8 \text{ mdd}$$

From the value for k_3 and the intercept of the straight line of Fig. 4, the entropy and free energy of activation for the process were calculated to be

$$\Delta S^\ddagger = 19.7 \text{ cal/deg mole}$$

$$\Delta F^\ddagger = 13.4 \text{ kcal/mole}$$

Effect of chloride ion concentration.—As a check on the final term in the denominator of the reaction rate expression (XIV), a qualitative chloride ion dependence was determined. The results obtained are shown in Fig. 5.

TABLE II. Average rate data used in evaluation of rate equation

Solution pH	H ⁺ (mole/liter)	O ₂ (mole/liter)	Measured rate	
			c/m/dm ² 10 ⁶ corrosion	mg/dm ² day
2.66	0.00219	7.6 × 10 ⁻⁴	87	272
2.19	0.00645	7.6 × 10 ⁻⁴	245	767
		1.6 × 10 ⁻⁴	162	507
1.88	0.0132	7.6 × 10 ⁻⁴	294	921
1.66	0.0219	7.6 × 10 ⁻⁴	450	1410
		1.6 × 10 ⁻⁴	332	1040
0.84	0.145	7.6 × 10 ⁻⁴	705	2210

Temperature 45°C, rates are per dm² true surface area, measured electrolytically.

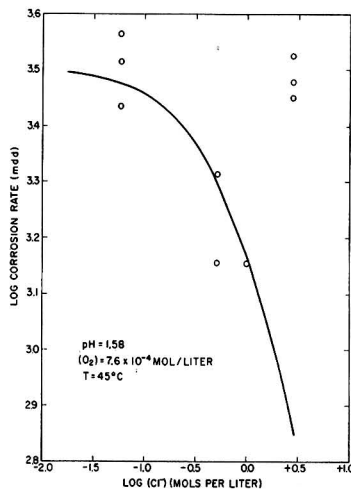


FIG. 5. Effect of chloride ion concentration on the corrosion rate.

It can be seen that the general behavior of the corrosion rate is as predicted over a range of concentrations 0.05N–1N. The previously discussed corrosion in the absence of oxygen would, *a priori*, be second order with respect to the chloride ion concentration; perhaps this process contributes appreciably to the reaction rate in the solutions 3N in chloride ion, and causes the observed rate increase.

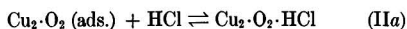
DISCUSSION

In evaluating the kinetic data, many surface reaction sequences were considered. However, only a double adsorption mechanism of the type described herein yields a reaction rate equation consistent with all of the experimental results.

A typical corrosion rate from this investigation, for comparison with earlier published results, is 190 mdd at 25°C in N KCl solution at a pH of 1.20, the solution saturated with oxygen at 650 mm Hg pressure, and a surface roughness of 5. This corresponds to about 900 mdd when the rate/dm² of geometric area is considered. This is the rate at steady-state conditions, and does not take into account the very much faster rate during the first few seconds.

Part of the large amount of corrosion products that appeared during the first few seconds might be considered in terms of the proposed mechanism to represent corrosion during establishment of the steady state. During the first few seconds, the metal surface rapidly becomes covered with adsorbed oxygen. Thus, initially, there are a large number of oxidized sites uncovered by any adsorbed acid. These could then readily be discharged according to reaction step (III). The electroreduction curves obtained by Hill (1) on copper cathodes cleaned in an identical manner suggest that the surface was initially oxide-free. However, were it not, a rapid dissolution of surface oxide might be expected upon dipping the sample into the acid solution. Part of the rapid initial solution rate may thus be attributable to the surface oxide.

The value of the free energy for hydrogen ion adsorption as calculated from the experimentally determined equilibrium constant K_2 is 2.5 kcal/mole. This is much too small a potential to represent any appreciable bonding between the ion and the "oxidized site." Since the chloride ion is suspected also to adsorb on the oxidized sites jointly with the hydrogen ion, ion pair adsorption is indicated. However, all solutions were 1*N* in chloride ion concentration; therefore, the value of K_2 and, thus, of the adsorption energy is not changed by this consideration. Recently, Hackerman and Stephens (21) have reported that sulfate ions chemisorb from solution on metallic iron in the presence of oxygen. They also found that the presence of chloride ions decreases the amount of sulfate adsorption from solutions of equal concentrations. Thus the chloride ion, or some derivative of it, apparently chemisorbs also on clean iron surfaces. Very possibly it also chemisorbs on clean copper surfaces. The equilibrium reaction K_2 possibly represents a true adsorption equilibrium since the adsorbed product is not removed by subsequent steps (as are the oxidized sites). A possible explanation of the low magnitude of the calculated adsorption potential, in view of the suggested chemisorption, is that the hydrogen and chloride ions do not adsorb as ion pairs but rather as the free hydrochloric acid molecule. In this case the reaction becomes



The concentration of the neutral hydrochloric acid molecules in solution is less than that of hydrogen ions by a factor of 10^7 . Thus, the adsorption energy becomes 12 kcal/mole, a much more reasonable value for explaining the observed effects.

The concept of adsorption of neutral acid or base molecules has been successfully used by Cook and co-workers (22-26) to explain other experimental results. It may possibly be applicable also in this system.

ACKNOWLEDGMENT

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1956 JOURNAL.

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Oxidation of Aluminum in the Temperature Range 400°–600°C

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ABSTRACT

The surface oxidation kinetics of metallographically polished high purity aluminum were studied in the temperature range 400°–600°C using a vacuum microbalance technique. The oxidation rate of aluminum decreased to a low value after a formative stage of film growth which was governed by a parabolic law. Values of the activation energies of reaction were determined from the temperature coefficient of the parabolic law constants and were compared with other values reported in the literature. By attaching equal significance to gaseous and anodic oxidation results, a value of 37.2 kcal/mole (1.6 ev) was determined for the potential energy barrier against ion diffusion at the metal/oxide interface.

INTRODUCTION

Most workers in the field of surface oxidation of aluminum hold the view that this metal forms a thin oxide film. Film thicknesses of 10–30Å at room temperature have been measured (1–6). Measurements by Cabrera and Hamon (3), Hass (4), and Treadwell and Obrist (7) have shown that the film thickness does not exceed 200Å at temperatures up to 300°C. In the temperature range 500°–600°C oxidation virtually ceased at a film thickness of approximately 2000Å (8, 9).

Reaction kinetics have been treated quantitatively by Gulbransen and Wysong (10) who found that the oxidation rates of aluminum obeyed a parabolic law in the temperature range 350°–475°C, with an activation energy and entropy of reaction of 22.8 kcal/mole and of –25.4 to –28 eu, respectively. Above 475°C, the reaction deviated from the parabolic rate law. Although these oxidation tests were carried out for only 2 hr, general conclusions have been drawn concerning the reaction kinetics. Many authors have not conceded the virtual cessation of oxidation at elevated temperatures, and believe that aluminum exhibits a parabolic or parilinear law of oxidation. Also, the value of 22.8 kcal/mole for the activation energy of reaction is inconsistent with a value of 37–42 kcal/mole determined by Charlesby (11) from anodic oxidation results. Hence, in this investigation the studies of Gulbransen and Wysong (10) have been extended to elucidate the reaction kinetics; this was accomplished by completing oxidation tests for exposures of 24 hr in the temperature range 400°–600°C.

EXPERIMENTAL

Apparatus

A vacuum microbalance assembly similar to that described by Gulbransen (12) was employed for the kinetic measurements. The quartz microbalance was used for following weight changes; this was done by observing pointers on the balance beam and frame with a sliding

microscope. The balance sensitivity was 1 division (0.001 cm) of the micrometer slide per 3.4 µg for a sample and counterweight of 0.6800 g. The micrometer readings were estimated to one-fourth of a division which represented 5Å of film thickness for the 5 × 2 cm specimens taken. This is valid on the assumption that the oxide film density is 3.4 for gamma-alumina and the surface roughness ratio is unity.

The vacuum system was of conventional design and consisted of pressure gauges, oxygen purification train and storage, microbalance container, triple stage oil diffusion pump, and other standard accessories. All openings in the vacuum manifold to the microbalance were larger than 12 mm diameter in order that specimens could be degassed rapidly in a vacuum of 10⁻⁶ mm. A liquid air trap was placed between the balance container and the vacuum manifold to protect the metal specimens from reaction with mercury vapor.

The furnace, which was positioned about the quartz microbalance tube by a counterweight, consisted of a 12 in. × 1 in. diameter McDanel combustion tube wound with a monel heating element and insulated by vermiculite in an aluminum container. Two iron-constantan thermocouples were set in the lower end of the combustion tube, one of which was connected to a Minneapolis Honeywell temperature indicating controller with electropulse duration control; the other one was connected to a potentiometer for setting and checking temperatures. The temperature in the region for metal specimens was determined by attaching a calibrated iron-constantan thermocouple to a metal specimen suspended in position in the quartz reaction tube. Temperatures were controlled to ±1°C.

Materials and Their Preparation

Specimens were prepared from a 4 in. × 1¼ in. cylinder machined from super purity aluminum of impurity contents: iron, 0.002%; copper, magnesium, 0.001%; boron, beryllium, bismuth, calcium, chromium, gallium, man-

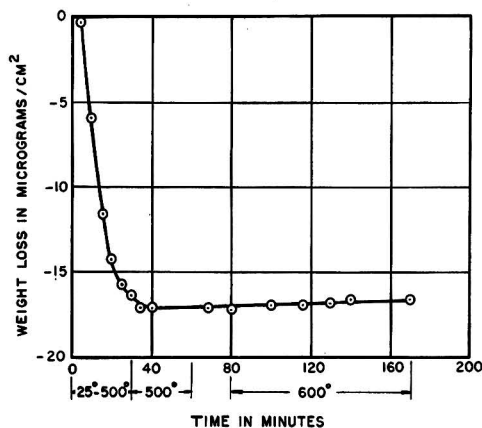


Fig. 1. Degassing of metallographically polished aluminum.

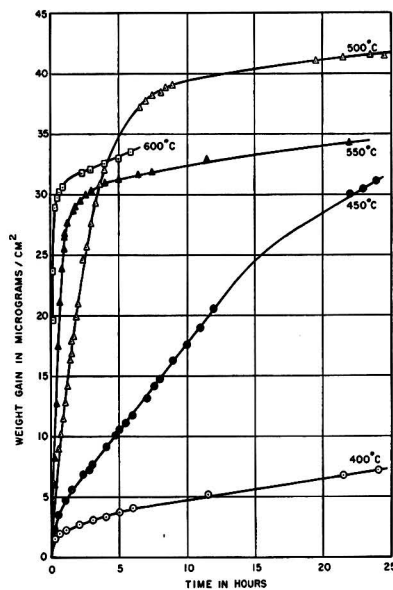


Fig. 2. Oxidation tests 400°-600°C, metallographically polished specimens degassed at 500°C.

ganese, nickel, silicon, sodium, titanium, tin, lead, vanadium, zirconium less than 0.001%. This cylinder was melted, degassed, and solidified in a vacuum of 10^{-6} mm after which the surface was scalped. The slug was then cold rolled to a thickness of 0.12 in., annealed for 30 min at 550°C and given a final cold reduction of 0.01 in. thickness. This sheet was stored in a desiccator.

Specimens were cut from the sheet and polished metallographically with emery papers 0, 00, and 000, respectively, with the last polish completed under a solution of paraffin in kerosene. Specimens were given a final polish with a dry Selvyt cloth to remove polishing material embedded in the metal surface, cut into $5\frac{1}{2} \times 2$ cm strips, and stored in a desiccator. For oxidation tests, specimens were trimmed to a weight of 0.6800 g.

Oxygen was purified by passing commercial cylinder oxygen through a train consisting of Ascarite for removal of carbon dioxide, heated platinum for oxidation of hydrogen and carbon monoxide, phosphorous pentoxide for removal of water, and a liquid air trap for removal of residual condensable vapors.

Procedure

A specimen was degassed carefully before oxidation by subjecting the specimen to a vacuum of 10^{-6} mm at room temperature for 5 hr and at 500°C for a further 30 min. The furnace was set then at a temperature for an oxidation test or for a further vacuum anneal at 500° or 600°C.

Oxide film formation on aluminum was studied as a function of time and temperature at 7.6 cm oxygen pressure. This pressure was chosen for experimental convenience since the rate of oxidation of aluminum is largely independent of pressure (10). In the first group of oxidation tests, the specimens were vacuum annealed for 30 min at 500°C and exposed in the temperature range 400°-600°C. In the second group of oxidation tests, the specimens were vacuum annealed 1 hr at 600°C and exposed in the temperature range 400°-600°C.

RESULTS AND DISCUSSION

Vacuum degassing.—A typical degassing curve is illustrated in Fig. 1. Evolution of gas was slow below 200°C but with higher temperatures, gas evolved rapidly with complete degassing of the specimen taking place after heating for 30 min at 500°C. The weight loss of $17 \mu\text{g}/\text{cm}^2$ represented a gas content of 500 ppm. The degassing curve showed that under a vacuum of 10^{-6} mm the specimen exhibited a slow weight increase due to the gettering property of aluminum at elevated temperatures.

Oxidation tests.—Fig. 2 shows oxidation curves at various temperatures in the range 400°-600°C for specimens vacuum annealed 30 min at 500°C. The manner in which the oxide film grew on the aluminum specimens was similar at all elevated temperatures, i.e., there was an initial rapid rate of oxidation which was followed by an approximately constant rate of film growth for a period which was dependent on the temperature. After this formative stage, the rate of oxidation fell off to a low value. Consideration of the curves in Fig. 1 for the 400°-500°C range suggests that there is some justification for a prevalent view that the oxidation rates of aluminum obey a parabolic law in the temperature range 350°-475°C and a linear law at higher temperatures. The curves are parabolic in form for the two lower temperatures and approximately linear in form at 500°C. However, the oxidation curves at the higher temperatures of 550° and 600°C limit this view of parabolic oxidation to specific regions of film thickness. This is also borne out by data presented in a previous publication (13).

Annealing the specimen in vacuum at elevated temperatures altered its oxidation characteristics (13). It was found that the oxidation rate of metallographically polished aluminum at 500° was dependent on the temperature and time of vacuum annealing of the specimens. Specimens annealed at 600°C oxidized less rapidly than

those annealed at 500°C. The specimen which had undergone a longer vacuum anneal at 500°C had a lower rate of oxidation. Also, specimens vacuum annealed at 600°C for 1 and 2 hr oxidized less rapidly than did a specimen annealed for 30 min at 600°C. These decreases in oxidation rates due to vacuum annealing may be caused by alteration of the initial surface oxide film present on the aluminum from amorphous to crystalline oxide or by a change in defect and dislocation concentration. This conclusion is borne out by the work of De Brouckère (14) who showed by electron diffraction that after 6 hr of heating at 400°C and after 1 hr of heating at 500°C, gamma-alumina forms in the oxide film on metallographically polished aluminum, and it forms after 1 min on the surface of molten aluminum.

The final film thicknesses illustrated in Fig. 2 for 550° and 600°C were less than the film thickness at 500°C. This anomaly may be due to the formation of crystalline oxide at these higher temperatures during the degassing stage since adjustment of the temperature at 550° or 600°C required 30 min after the vacuum anneal at 500°C.

In view of this influence of vacuum annealing, oxidation tests, illustrated in Fig. 3, were carried out using specimens vacuum annealed 1 hr at 600°C. These curves are similar in form to those of Fig. 2. Oxidation rates of samples annealed at 600°C, however, were less at 400°, 450°, and 500°C due probably to the formation of a more crystalline film. At 550° and 600°C, initial oxidation rates were identical, but the rate of film growth decreased more slowly for specimens annealed at 600°C. The fact that initial oxidation rates at these latter temperatures are equal indicates that the film structure is essentially the same at these temperatures in spite of variations in the vacuum anneals. The final thickness of the film may be greater for specimens annealed at 600°C due to an increase in concentration of such surface impurities as copper and iron which have a detrimental effect on the protective properties of the oxide film (9, 15).

Experimental precision.—Individual oxidation curves for specimens removed from a small section of the sheet and vacuum annealed at 500°C were reproducible within 10%. In the case of specimens vacuum annealed at 600°C for 1 hr, the oxidation tests at 500°C exhibited a greater deviation. An explanation of this effect is not possible unless extensive diffraction studies are undertaken of film structures in situ and the effects of impurities on oxidation rates determined.

OXIDATION MECHANISM

No oxidation rate law satisfies the experimental results over all ranges of film thickness. Although deviations exist, the concept of diffusion-controlled parabolic oxidation is probably the best approach and is therefore employed in this analysis. That this is the most reasonable choice is borne out first by Cabrera, Mott, and their co-workers (2, 3, 16–22) who postulate that the surface film on aluminum consists of a "metal-excess" oxide and that film growth occurs by diffusion of metallic ions through lattice interstitial positions; and second by Charlesby (11, 23) who has demonstrated that this theory is applicable to the anodic oxidation of aluminum. According to their views, the kinetics of gaseous oxida-

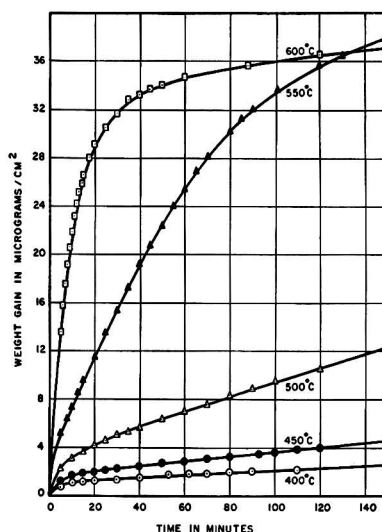


FIG. 3. Oxidation tests 400°–600°C, metallographically polished specimens degassed at 600°C.

tion of aluminum should be governed by a parabolic law in the temperature range 400°–600°C.

The equation for the parabolic law of oxidation is:

$$x^2 = Kt + C \quad (\text{I})$$

where x is the film thickness, t is the time, K is the parabolic rate constant, and C is a constant representing the initial film thickness.

Cabrera and Mott (2) showed that this law is applicable to the growth of both thin and thick films. The parabolic rate constant for a thin film is:

$$K = \frac{V\Omega q_i}{a_i} \frac{\gamma}{kT} \exp - W/kT \quad (\text{II})$$

and for a thick film:

$$K = 2\Omega(N_i N_e)^{1/2} a_i^2 \gamma \cdot \exp - \frac{1}{2}(W_i + \phi) - U/kT \quad (\text{III})$$

Here W and ϕ are the potential energy barriers at the metal/oxide interface against ion and electron diffusion, respectively, W_i and U are the potential energy barriers between ion diffusion states from metal to oxide and between interstitial positions in the oxide, respectively, N_i and N_e are the concentrations of interstitial positions in the oxide and electrons in the metal, respectively, V is the potential across the oxide film, Ω is the volume of oxide per metal ion, q_i is the electrical charge of the metallic ion, γ is the frequency of vibration of the oxide lattice, a_i is the half-width of the potential barrier against ion diffusion, k is Boltzmann's constant, and T is the absolute temperature.

Gulbransen (24) has applied transition state theory to express the parabolic rate constant by the equation:

$$K = \frac{2kT\lambda^2}{h} \exp \frac{\Delta S^*}{R} \exp - \frac{E}{RT} \quad (\text{IV})$$

where E and ΔS^* are the activation energy and entropy

of reaction, respectively, k is Boltzmann's constant, R is the gas constant, h is Planck's constant, and λ is the interatomic distance between diffusion sites.

Fig. 4 shows the experimental results at 550°C plotted on a parabolic scale, i.e., $(\text{g}/\text{cm}^2)^2$ vs. time. This curve shows an initial linear section which undergoes transition to a second linear section of greater slope and this, in turn, gives way as exposure time increases to a section with lower slope. This type of curve is obtained at all temperatures in the region 400°–600°C with the duration of each linear section dependent on the temperature. It is arbitrarily assumed that these linear sections of the curves yield the values of the parabolic rate constants for the thin and thick film ranges. These constants are recorded in Tables I and II.

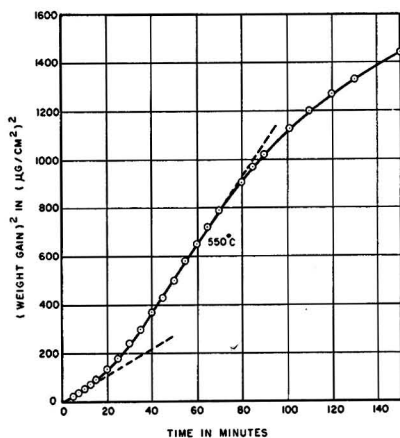


FIG. 4. Parabolic plot of oxidation data for specimen degassed at 550°C.

Parabolic oxidation rate constants are expressed in Arrhenius form:

$$K = Ae^{-E/RT} \quad (V)$$

where A is the frequency factor and E is the energy of activation.

Fig. 5 shows plots of $\log K$ vs. $1/T$ for specimens vacuum annealed at 500°C; a similar linear plot was obtained for specimens vacuum annealed at 600°C. The frequency factors and energies of activation with a

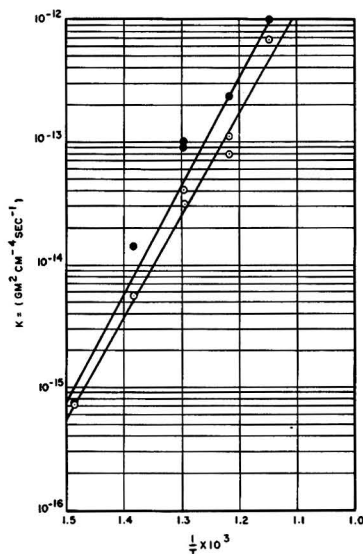


FIG. 5. Arrhenius plots of parabolic rate constants for specimens degassed at 550°C. ○—Thin film; ●—thick film.

TABLE I. Parabolic rate constants, energies, and entropies of activation for the oxidation of metallographically polished aluminum degassed for 30 min at 600°C

Temp, °C	1st Section of parabolic plot				2nd Section of parabolic plot			
	K (g/cm²)²/sec	A g²cm⁴sec⁻¹	E cal/mole	ΔS^* cal/degree mole	K (g/cm²)²/sec	A g²cm⁴sec⁻¹	E cal/mole	ΔS^* cal/degree mole
400	7.2×10^{-16}	1.6×10^{-3}	37,900	-7.1	7.5×10^{-16}	1.7×10^{-2}	40,500	-3.2
450	5.5×10^{-15}		37,900	-7.2	1.4×10^{-14}		40,500	-1.7
500	3.3×10^{-14}		37,900	-7.1	1.0×10^{-13}		40,500	-1.5
	4.0×10^{-14}		37,900	-6.7	8.9×10^{-14}		40,500	-1.8
550	7.9×10^{-14}		37,900	-8.4	2.4×10^{-13}		40,500	-3.1
	1.1×10^{-13}		37,900	-7.7	2.3×10^{-13}		40,500	-3.2
600	6.8×10^{-13}		37,900	-7.0	1.1×10^{-12}		40,500	-3.2

TABLE II. Parabolic rate constants, energies, and entropies of activation for the oxidation of metallographically polished aluminum degassed for 1 hr at 600°C

Temp, °C	1st Section of parabolic plot				2nd Section of parabolic plot			
	K g²cm⁴sec⁻¹	A g²cm⁴sec⁻¹	E cal/mole	ΔS^* cal/degree mole	K g²cm⁴sec⁻¹	A g²cm⁴sec⁻¹	E cal/mole	ΔS^* cal/degree mole
400	6.7×10^{-16}	8.0×10^{-3}	41,000	-2.7	2.4×10^{-15}	6.0	50,700	8.9
450	1.9×10^{-15}		41,000	-5.0			2.6×10^{-14}	50,700
500	1.3×10^{-14}		41,000	-5.0	2.3×10^{-13}		50,700	9.3
550	1.2×10^{-13}		41,000	-3.8	9.6×10^{-13}		50,700	8.4
600	6.0×10^{-13}		41,000	-3.7				

precision of ± 5000 cal/mole are tabulated in Tables I and II. Energies of activation of 37.9 and 41.0 kcal/mole for the first linear section of the parabolic plots represent $W_i + U$ [equation (II)], and energies of activation of 40.5 and 50.7 kcal/mole for the second linear section represent $\frac{1}{2}(W_i + \phi) + U$ [equation (III)], if the considerations of Mott and Cabrera are valid. These values of the activation energies, which are larger in the thick film range, do not substantiate their suggestion that the increase in the parabolic rate constant is caused by a decrease in the activation energy by assuming that $W_i > \phi$.

Equation (IV) was used to calculate, arbitrarily, values of the entropy of activation for the two linear sections of the parabolic plots with the assumption that the interatomic jump distance for diffusion was 3.74 Å. Values of this term are recorded in Tables I and II. Two conclusions are apparent: the entropy of activation is negative and becomes of smaller negative value with increasing film thickness and this value is more positive for specimens vacuum annealed at the higher temperature of 600°C. Gulbransen (25) suggested that large negative values indicate the presence of short-circuiting diffusion paths around the grain boundaries. This view has been questioned by Moore (26) for aluminum because the crystalline size in the amorphous oxide is so small that no electron diffraction pattern has been observed. Since Wilsdorf (27) has interpreted the diffraction photographs of the amorphous oxide film as consisting of totally disordered Al_2O_3 molecular groups, diffusion may occur at elevated temperatures by paths around and through aggregates of these molecular groups. The fact that the entropy of activation becomes more positive for longer exposure times and for specimens vacuum annealed at the higher temperature of 600°C indicates that those molecular groups, within themselves bound by ionic forces, become larger by crystallization and remove short-circuiting paths. Support for these views on the effect of crystallization is found in a reduction of oxidation rates of aluminum vacuum annealed for relatively longer times and higher temperatures.

Kinetic measurements, alone, do not aid substantially in elucidating the mechanism of the high temperature oxidation of aluminum. The concept of diffusion-controlled parabolic oxidation has stringent limitations because no account is taken of variations in crystalline structure of the oxide film. In an attempt to place the experimental data within this theoretical framework, two arbitrary assumptions have been made, namely, that oxidation rate constants can be determined from finite linear sections of the parabolic law plots and that these constants obey the Arrhenius relation, although crystallization of oxide is occurring simultaneously with film growth.

Literature Assessment

The activation energy of reaction in the thin film range represents, according to the Mott and Cabrera theory, the potential barrier against ion diffusion at the metal/oxide interface. Values for this barrier of 37.9 and 41.0 kcal/mole (1.6 and 1.8 ev) from this investiga-

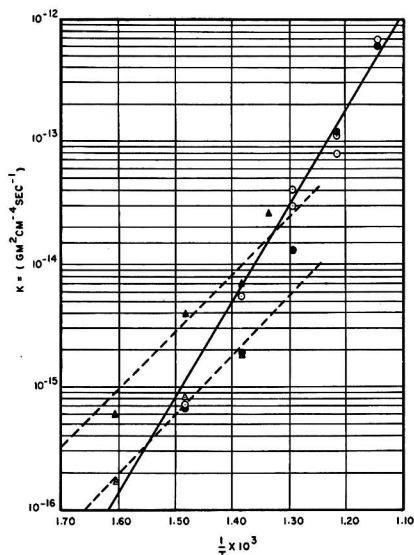


FIG. 6. Arrhenius plots of parabolic rate constants for thin oxide film. Δ , \triangle —Determinations by Gulbransen and Wysong; \bullet , \circ —determinations of this investigation; -----Gulbransen and Wysong plot; ————root mean square plot.

tion are in excellent agreement with values of 1.6 and 1.8 ev determined by Charlesby (11) from results on the anodic oxidation of aluminum. These values are inconsistent with a determination of 22.8 kcal/mole by Gulbransen and Wysong (10) from high temperature gaseous oxidation studies. These investigators found large variations in oxidation rates for two samples of high purity aluminum and interpreted the data separately for each sample. Plots of $\log K$ vs. $1/T$ for parabolic rate constants of their investigation and those for the initial stage of parabolic oxidation of this study are shown in Fig. 6. Because of the broad scatter of experimental values the root mean square value of the activation energy may be most appropriate for determination of the barrier against ion diffusion. Accordingly, the value of the parabolic rate constant for the high temperature oxidation of aluminum in the thin film range is:

$$K(g^2 \text{ cm}^{-4} \text{ sec}^{-1}) = 6.33 \times 10^{-5} \exp - 33,100/RT$$

A mean value of 37.2 kcal/mole (1.6 ev) is obtained for the potential barrier against ion diffusion at the metal/oxide interface if the same significance is attached to the two determinations from anodic oxidation data and this root mean square value of the energy of activation.

SUMMARY

Reactions of aluminum with oxygen have been studied, using a vacuum microbalance technique, over the temperature range 400°–600°C. At all temperatures there was an initial rapid rate of oxidation which was followed by an approximately constant rate of film growth for a period dependent on temperature. After this formative

stage, the rate of oxidation decreased to a negligible value. Vacuum annealing metallographically polished aluminum in the temperature range 500°-600°C caused formation of an oxide film which was more resistant to oxidation.

Reaction rate results were interpreted according to a parabolic law of oxidation. Values of 37.9 and 41.0 kcal/mole were determined for the activation energy of reaction in the thin film range for specimens vacuum annealed at 500° and 600°C, respectively. A mean value of 37.2 kcal/mole was obtained for the energy barrier against ion diffusion at the metal/oxide interface by attaching equal significance to results from gaseous and anodic oxidation. An increase in the magnitude of the energy of activation at larger film thickness and the cessation of oxidation have emphasized the limited applicability of present theories in explaining the high temperature oxidation mechanism of aluminum.

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The Voltage Drop Through Phosphor Screens and Its Bearing on Performance of Cathodoluminescent Lamps

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ABSTRACT

Measurements have been made of the voltage drop when an electron beam passes through a fluorescent screen. This varies from a few volts to several hundred volts depending on the nature of the phosphor. By choosing phosphors with high conductivity, the major part of the voltage drop across an electron tube is made available for excitation of the phosphor. This principle is applied to the construction of 120-volt cathodoluminescent lamps.

INTRODUCTION

The efficiency of light production in many cathode ray and television tubes, although of less importance than the brightness of the cathode spot, may be fairly high. Values of 24% radiation efficiency at 20 kv have been reported by Brill and Klasens (1) and a luminous effi-

ciency of 98 lpw has been obtained with phosphors such as ZnCdS:Ag where the emission band is in the middle of the visible spectrum. These values are sufficiently high to make cathode ray excitation attractive as a source of illumination. The disadvantages of lamps operating in the kv range are obvious. Accordingly, it

seemed worthwhile to investigate the possibilities of cathode ray excitation at ordinary commercial voltages, say 120 v.

When the voltage for cathode ray excitation is lowered from several kilovolts to some tens of volts, three limitations which are of little importance at the higher voltage must be considered. These are: (a) the "dead voltage;" (b) the first "crossover" for secondary emission; (c) the voltage drop through the phosphor screen.

The relation between voltage and brightness for phosphors is of the form $L = Af(i)(V - V_0)^n$, where L = luminescence emission, i = current density, V = applied anode voltage, V_0 = "dead layer voltage," n = a constant, usually in the range from 1 to 3. V_0 , the dead voltage is interpreted as the voltage required to penetrate an inert nonluminescent layer on the surface of the phosphor grains. It is usually of the order of a few tens to a few hundreds of volts. It is just in this range that it would be desirable to operate cathode ray lamps. Accordingly, the dead voltage results in a considerable decrease in efficiency as anode potential is reduced to the low voltage (120 v) region. Attempts have been made to remove the dead layer by chemical treatment (2), but no study has been made of the effectiveness of this treatment at low voltage.

The second effect which limits the excitation of phosphors at low voltages is the secondary electron emission from the phosphor. In most cathode ray tubes the phosphor is prevented from charging up by the emission of secondary electrons. Unless the number of secondary electrons emitted is equal to the number of incident electrons the phosphor rapidly charges up to cathode potential. The number of secondaries emitted per incident primary is a function of the primary voltage. Below a critical voltage known as the "first crossover" the number of secondaries per primary becomes less than unity and a tube with a phosphor on an insulating surface becomes inoperative. For many phosphors the first crossover is between 50 and 200 v which again is just in or above the range in which we wish to operate lamps.

An alternative method of discharging the phosphor is to apply it to a conducting anode so that the charge can leak off the phosphor to the anode. This results in a voltage drop through the screen. It was the purpose of this investigation to measure the voltage drop through phosphor screens and to find out what bearing this had on the operation of cathode ray lamps.

Some measurements were made to select phosphors of various resistances for these tests. The measurements were made on 0.5 g cylindrical pellets of the various phosphors pressed in a hand press using a die, 0.3 in. in diameter. Contact was made with brass electrodes by dusting a little metallic zinc powder on the bottom of the die and on top of the powder, before pressing. The height of the pellets was 2 mm or more depending on the density of the powder. Materials such as ZnO and Zn_2SiO_4 made compact durable pellets, while those of ZnCdS were very fragile. Values of resistance were measured in vacuo with a megohmmeter which impressed 10-20 v across the sample. The phosphors tested and the measured resistances of the pellets are listed in Table I. In spite of the variation

TABLE I. Resistance measured in vacuo with megohmmeter and 10-20 v impressed across sample

Resistance of phosphor pellets Phosphor	Resistance of 0.5 g pellet in vacuo
ZnO:Zn (N.J. Zinc Co. No. 2100)	$0.4 \times 10^6 \Omega$
ZnO:Zn (N.J. Zinc Co. No. 2100)	$60 \times 10^6 \Omega$
ZnO:Zn (N.J. Zinc Co. No. 2100)	$20 \times 10^6 \Omega$
ZnO:Zn (N.J. Zinc Co. No. CE4107)	$55 \times 10^6 \Omega$
Zn_2SiO_4 :Mn (GE Co.)	$>5 \times 10^{10} \Omega$
ZnS:Ag (Patterson No. 1410)	$>5 \times 10^{10} \Omega$
CaMg (SiO ₃) ₂ :Ti (Sylvania No. 270)	$>5 \times 10^{10} \Omega$
Ca ₃ (PO ₄) ₂ :Ce	$>5 \times 10^{10} \Omega$
CaO:Pb (Fonda)	$>5 \times 10^{10} \Omega$
ZnS:Zn (Prener)	$>5 \times 10^{10} \Omega$
ZnCdS:Ag (90% Cd)	$>5 \times 10^{10} \Omega$
ZnS:Se:Cu (GE Co. 3-310)	$>5 \times 10^{10} \Omega$
ZnO:MgO (N.J. Zinc Co. No. 2115)	$>5 \times 10^{10} \Omega$
Mg Titanate (N.J. Zinc Co. No. 2125)	$>5 \times 10^{10} \Omega$
CdS:Ag (Fonda)	$>5 \times 10^{10} \Omega$

in compactness of the powder in the various pellets, it was evident that zinc oxide phosphor had a conductivity higher by at least three orders of magnitude than 12 other common phosphors tested.

The zinc oxide phosphor used was much finer grained than the other phosphors. It showed the well-known increase in resistance due to adsorption of O₂ which has been studied by Morrison (3). One sample dropped from $10^6 \Omega$ at one atmosphere to $4 \times 10^6 \Omega$ in vacuo in about 3 hours' time. This effect was completely reversible.

SCREEN VOLTAGE DROP MEASUREMENTS

With this information as a guide, the voltage drop through a number of different phosphor screens was studied in a special form of cathode ray tube. Some of these screens consisted essentially of monolayers of grains and had no binder (4). The average coating weight for screens of this kind is less than 2 mg/cm². Several screens, settled by the conventional liquid settling process, using Kasil binder, were also tested, as well as one deposited by the Studer and Cusano (5) vapor reaction process. The phosphors and the coating weights are listed in Table II.

The tube contained a simple electron gun which focused a beam of electrons on the phosphor screen, a coarse mesh grid to collect secondaries, and a phosphor screen deposited on a surface of conducting glass with which contact was made by a wire sealed through the glass. A moveable shutter over the end of the anode prevented barium from depositing on the screen during activation of the cathode. The tube construction is shown schematically in Fig. 1. A fixed potential of 200 v was applied to the first anode and to the grid. This gave a beam current of approximately 1 ma to the anode (screen) and a spot about 1 cm in diameter.

The relation between anode current and anode voltage for a tube with a conducting glass anode (and no phosphor coating) is shown in Fig. 2, curve *a*. The current saturates at about 10 v. At higher voltages the anode current decreases, as shown by the dotted line, because of secondary emission from the anode. However, we are not concerned with this part of the curve. The volt ampere curve up to saturation shows the relation for this geometry

TABLE II. Voltage drop through phosphor screens

Phosphor	Screening procedure	Estimated thickness	Voltage drop at	
			$1 \mu\text{a}/\text{cm}^2$	$100 \mu\text{a}/\text{cm}^2$
ZnO:Zn (N.J. Zinc Co. No. 2100)	Monoparticle layer	μ	<1	<1
ZnS:Zn (Prener)	Monoparticle layer	5	10	130
ZnCdS:Ag (65% Zn, 35% Cd)	Monoparticle layer	5	4	27
Zn ₂ SiO ₄ :Mn (GE)	Monoparticle layer	5	34	220
ZnS:Ag (Patterson No. 1410)	Monoparticle layer	5	2	27
ZnS:Mn	Vapor reaction film	8.5	—	30
ZnO:Zn (N.J. Zinc Co. No. 2100)	Liquid settled	5	9	65
Zn ₂ SiO ₄ :Mn (GE)	Liquid settled	5	13	240
Zn ₂ SiO ₄ :Mn (GE)	Liquid settled	10	26	420

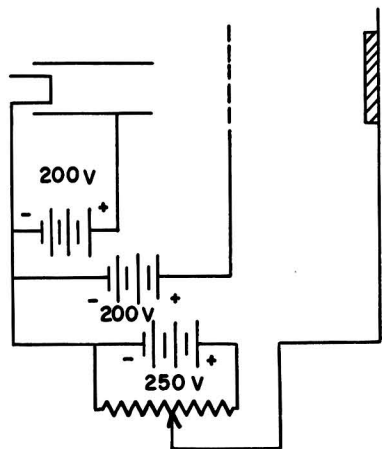


FIG. 1. Schematic diagram of tube for measurement of screen characteristics.

between beam current and the potential of the surface of the anode. Fig. 2, curve *b* shows the anode volt ampere relation for a tube of identical construction, differing from the first only in that the anode has a phosphor coating. Curve *b* is displaced to the high voltage side of curve *a* by an amount corresponding to the voltage drop through the phosphor, the voltage drop through the space being given the abscissas of curve *a*.

From data such as these, curves of current through the screen vs. voltage drop across the screen for various phosphors can be constructed. These curves are all of the same general form shown in Fig. 3, indicating a very high impedance for small currents which drops to a much smaller value with increasing current. The latter part of the curve fits an exponential of the form

$$i = Ke^{V/a}$$

where i = beam current, V = beam voltage, and K , a = constants. This part of the curve corresponds to average field strengths across the phosphor of 10^5 – 10^6 v/cm.

Table II shows the voltage drop measured by this method at two different values of current density. The higher current density approximates the value used in some low voltage cathode ray lamps to be described later. The table shows that the voltage drop at $100 \mu\text{a}/\text{cm}^2$ through monolayer phosphor screens is less than 1 v for the zinc oxide phosphor and from 27 to 220 v for the other four phosphors deposited in this way. The Zn₂SiO₄ shows the highest voltage drop. For thicker screens, the voltage drop increases roughly in proportion to screen thickness as is shown by the data on liquid settled Zn₂SiO₄:Mn. The drop through a 10 mg/cm² liquid settled Zn₂SiO₄:Mn screen at $100 \mu\text{a}/\text{cm}^2$ is 420 v.

CATHODE RAY LAMP CHARACTERISTICS

With information about the phosphor voltage drop, it is possible to predict the characteristics of cathode ray lamps. Consider a lamp consisting of a hot cathode at the center of a spherical bulb, the inside of the bulb having a transparent conducting coating on which the phosphor is

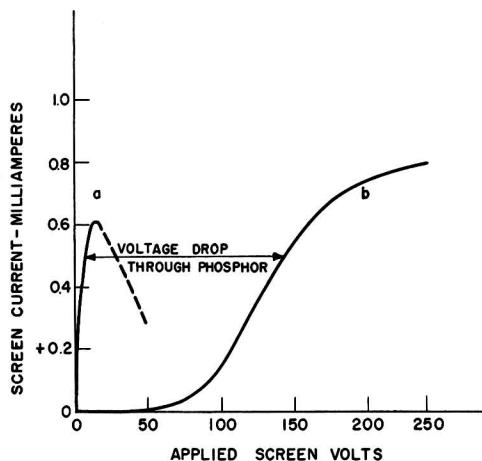


FIG. 2. Phosphor screen voltage-current relations

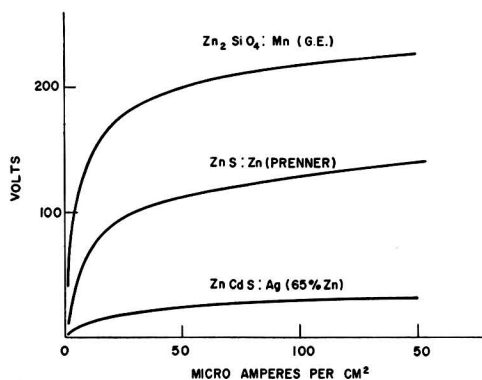


FIG. 3. Voltage drop through phosphor screens

deposited. Fig. 4 shows, on the left, the voltage current relation for this device as it would be if limited by the $3/2$ power space charge law only, that is, with no phosphor on the anode. On the right is shown the phosphor voltage current relation. The lamp will operate at a current determined by the intersection of these two curves. The applied voltage will be divided between the space and the phosphor in the ratio V_s to V_p . V_s is useful in accelerating electrons across the space and exciting luminescence. V_p is the voltage drop necessary for the passage of current through the phosphor and does not contribute to the luminescence.

Fig. 5 shows calculated lamp characteristics for three different phosphors. The phosphor voltage current relations were determined by the cathode ray tube method already described. The relation for the lamp without the phosphor was calculated from the $3/2$ power law. The heavy curve shows the characteristic for a 250-v lamp and the dashed curve shows it for a 120-v lamp.

From the figure it is evident that for a given lamp construction a high-resistance phosphor can only operate at a small current density with a relatively small fraction of the applied voltage available for excitation. With a low-resistance phosphor, on the other hand, the current is limited practically only by space charge and most of the applied voltage is available for excitation.

The applied voltage can be a very misleading criterion of phosphor brightness because the drop through the phosphor accounts for such a large fraction of the voltage. For instance, Fig. 5 shows that with 120 v applied to a lamp with a willemite screen, the drop through the screen accounts for 110 v, leaving only 10 v for acceleration of the electrons. Thus, the luminescence observed is due to 10-v electrons and not 120-v electrons.

A number of low voltage cathode ray lamps were constructed with various phosphors. These consisted of 3 in. Pyrex glass bulbs with SnO_2 conducting coatings on the inside walls and centrally located indirectly heated oxide coated cathodes. The cathodes were capable of supplying ample emission so that they were not a limiting factor in the operation of the lamps. The bulbs were coated on the inside wall with a nitrocellulose suspension of the phosphor. The nitrocellulose was burned out by baking in a stream of oxygen and the bulbs were then evacuated. Lamps with zinc oxide coatings were found to operate over any desired voltage range. Luminescence was uniform over the entire bulb and increased steadily in brightness from a threshold of a few volts. [Shrader and Kaisal (6) have shown a threshold for excitation of luminescence in zinc oxide of less than 3 v.] The volt ampere characteristic of the lamp with the phosphoric coating was almost the same as for the lamp with the conducting tin oxide coating only, showing that the voltage drop through the phosphor is negligibly small.

With Zn_2SiO_4 :Mn coatings, no luminescence was observed up to about 200 v where the lamp current was only a few microamperes. At this voltage a few small luminescent spots appeared. These shifted and grew in extent and brightness in a rather erratic manner with increasing voltage. This behavior is probably due to inhomogeneities or variations in thickness of different parts of the coating.

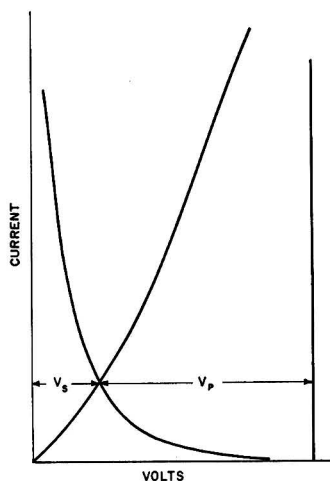


FIG. 4. Potential distribution in cathode ray lamp

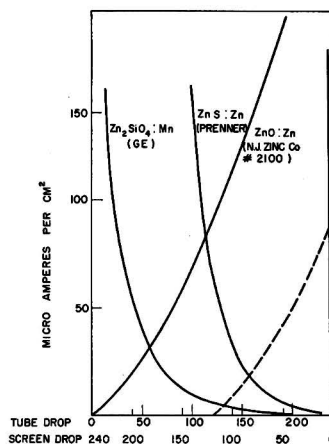


FIG. 5. Potential distribution in cathode ray lamps with various phosphors.

ZnS:Ag coatings gave considerably larger currents than Zn_2SiO_4 :Mn and above 100 v the lamps showed uniform luminescence over most of the bulb. Currents were about $1/10$ as large as for zinc oxide coatings. Thus, the characteristics of the lamps are in qualitative agreement with the characteristics predicted from measurements of the voltage drop through phosphor screens.

Since the screens studied in the cathode ray tube and those in the lamps were deposited by such different methods, quantitative agreement could not be expected.

From these experiments it was concluded that one of the most desirable properties in a phosphor to be used in low voltage cathode ray lamps is a high conductivity. The only available phosphor which meets this requirement [with the possible exception of ZnF_2 :Mn (7)] is ZnO:Zn .

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Five Metal Hydrides as Alloying Agents on Silicon

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ABSTRACT

The use of certain metal hydrides to promote alloying to silicon is described. Good ohmic contacts to both *n*- and *p*-type silicon have been made. The electrical resistance of a typical 1 cm² contact is less than 0.001 ohm. The depth of alloying may be controlled from 0.025 mm to 0.0025 mm depending on the alloy and the alloying temperature. Completed contacts exhibit tensile strengths in excess of 4500 psi.

INTRODUCTION

The use of silicon as a semiconductor involves the application of two or more electrical contacts to the silicon. These contacts may be rectifying or nonrectifying depending on what is used for the contact material and how the contact is made. Quite often a particular kind of contact can be made rectifying or nonrectifying by the addition of small amounts of donor or acceptor impurities to the contact material.

Alloying is the most satisfactory method of obtaining an intimate and permanent contact between any two materials. Tin-lead solder, one of the most commonly used contact materials in the field of electronics, depends on alloying to attain the very desirable electrical and mechanical properties usually associated with it. It is a rather common experience, however, to find that a flux is necessary in order to obtain good uniform wetting of most surfaces by solder.

In the case of silicon, the stable oxide film on the surface requires the employment of a more active flux for soldering than is used on common metals. Most of the conventional fluxes that are active enough to promote good soldering also leave corrosive residues. However, certain metal hydrides can be successfully employed as fluxes or alloying agents for silicon without producing corrosive residues. With such hydrides one product of their decomposition is hydrogen and the remainder is a metal which then forms part of the soldering alloy. In certain applications it may be necessary to add a small amount of impurity to the solder in order to obtain the desirable electrical properties.

This hydride method resembles a technique patented by Kelly (1) for making metal-ceramic seals. In such seals titanium hydride was used to obtain good wetting of a ceramic surface by a metal such as silver or copper. Heating in that case was done in a vacuum furnace. Other workers, including Cleveland (2), have extended this technique to

include other hydrides, some of which are more convenient to use than the titanium hydride.

Briefly, the hydride process as applied to silicon consists of coating the silicon with a thin film of the hydride and bringing this coated silicon surface into contact with the solder at an elevated temperature in an inert atmosphere. For convenience of application the powdered hydride may be suspended in an organic binder such as an amyl acetate solution of cellulose nitrate. The time in the furnace is of the order of 1-10 min; the atmosphere is nonoxidizing (nitrogen or hydrogen); and the temperature of the furnace may be 600°-900°C, depending on which hydride is employed.

Since the solder melts before the alloying temperature is reached, some provision must be made to hold the liquid solder in place while the assembly is being brought up to temperature. One method of accomplishing this is to dip the silicon specimen into the molten solder. Another method illustrated in Fig. 1 is the use of a pretinned metal cap. In this case the solder wets the cap and is held in place by surface forces. The choice between these two methods depends on the ultimate use of the contact. In many applications the retaining cap may be a structural part of the finished device, and the cap method would then be preferred. On the other hand, it may be impractical to submit certain portions of the device to the rather high temperature required for alloying and, in this case, the dipping technique plus a subsequent low temperature soldering operation is most convenient. The cap technique with the caps being made of Kovar was used for all of the data reported here.

HYDRIDES

A series of tests were made in which contacts were placed on opposite faces of thin slices of silicon, as shown in Fig. 1. The total resistance (*d-c* voltage/*d-c* current) of the structure was then measured and plotted against

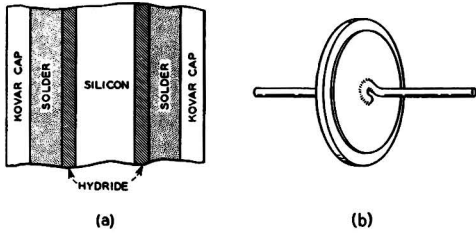


FIG. 1. (a) Section of assembly, not to scale; (b) completed test structure with leads attached for resistance measurements.

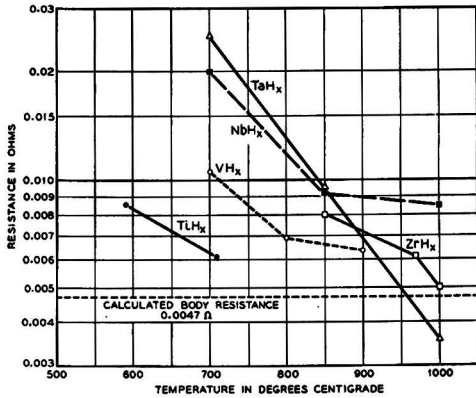


FIG. 2. Resistance as a function of alloying agent and temperature of alloying. Contact area is 1 cm².

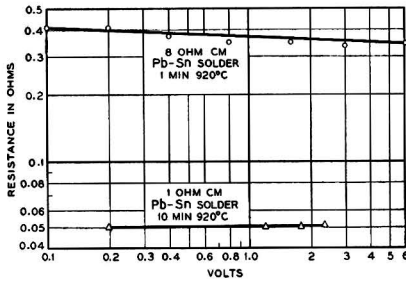


FIG. 3. Resistance as a function of voltage for two *n*-type silicon specimens, with zirconium hydride as alloying agent and a contact area of 1 cm².

the temperature of alloying for each of the five metal hydrides,¹ as shown in Fig. 2. The calculated body resistance is indicated by the dotted line. A minimum temperature of 600°-700°C must be employed before any alloying is obtained. At higher temperatures the contact is improved and the total resistance measured approaches the calculated body resistance. An examination of all six of the specimens which had been made with zirconium hydride indicated that the variation of resistance was due mainly to the fact that the surface was only partially wet at the lower temperatures of alloying. Even when only

¹ Hydrides were obtained from Metal Hydrides Inc., Beverly, Mass.

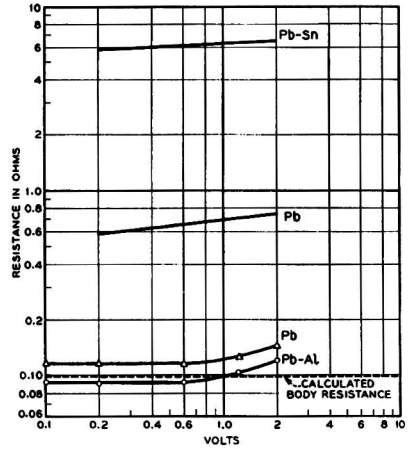


FIG. 4. Resistance as a function of voltage for 1 ohm-cm *p*-type silicon specimens, with zirconium hydride as alloying agent and a contact area of 1 cm².

TABLE I. Depth of penetration as a function of alloy and alloying agent. Heating time is 1 min

Solder alloy	Zirconium hydride at 900°C	Titanium hydride at 700°C
Pb.....	<0.0025 mm	<0.0025 mm
Pb-Sn (55:45)	0.01 to 0.015 mm	<0.0025 mm
Pb-Ga (98:2)	0.012 to 0.025 mm	<0.0025 mm

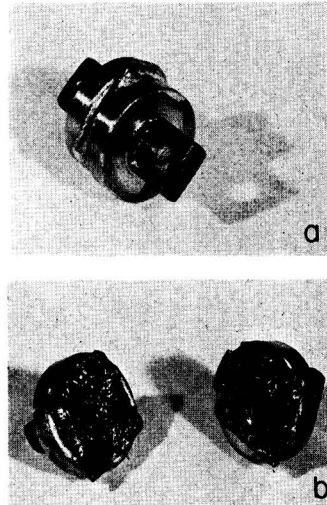


FIG. 5(a). Sample with heavy caps ready for tensile strength tests; Fig. 5(b). Sample after test showing the fractured silicon surface.

partial wetting occurred, however, the contacts were non-rectifying.

CONTACT TO *N*-TYPE SILICON

Contacts to *n*-type silicon are ohmic, as is indicated in Fig. 3. Here there are plotted the *d-c* resistances of two

test diodes as a function of voltage with silicon resistivity as the parameter. In both cases the observed resistance was so close to the calculated body resistance that no significant value could be assigned to the contact.

CONTACT TO P-TYPE SILICON

In the evaluation of the various hydrides previously described, low resistivity (0.038 ohm-cm) *p*-type silicon was used. From these data it would appear that good contacts may be easily made on low-resistivity *p*-type material.

With *p*-type silicon in the 1 ohm-cm range, however, appreciable contact resistance was observed as indicated in Fig. 4. The calculated body resistance of the diode is about 0.1 ohm but the measured resistance of a typical specimen is about 6 ohms when tin-lead solder is used, or about 0.6 ohm when pure lead (99.99 + %) is used. The contact resistance in this case would be about 6 ohms for the solder and 0.5 ohm for lead. The contact resistance is easily brought down to a negligible value, however, by doping the lead with about 1% aluminum as indicated by the circles, or by first providing a more heavily doped layer on the surface and then making a contact with pure lead as indicated by the triangles.

The necessity for doping the solder when used on *p*-type material but not when used on *n*-type suggests that a donor-type impurity may be present in the solder. An analysis of the alloy formed in the contact when tin-lead solder was used indicates the presence of antimony which is normally found in commercial solder. The antimony content can be reduced considerably by using a high purity lead in the tin-lead solder. In addition to the antimony there were appreciable percentages of iron, nickel, and cobalt. These presumably come from Kovar cap and may be eliminated if desired by the choice of another cap material, for example, molybdenum, or of no cap at all, in which case one may use the dipping technique mentioned previously.

DEPTH OF PENETRATION

For certain uses the depth of alloying may be important. The depth of penetration of the contact as a function of alloy composition and of alloying agent is given in Table I. Heating time in each case was 1 min. Penetration measurements were made by an optical examination of the sectioned contacts at a magnification of 500. The accuracy of the measurements was about ± 0.0025 mm. Penetration appears to be less than 0.0025 mm whenever lead is used as the solder or whenever the temperature is kept down to 700°C. On the other hand, for lead alloys at 900°C the penetration appears to be between 0.01 mm and 0.025 mm. Several of the other hydrides and other common flux materials were employed at the same temperature. The depth of penetration did not appear to be a function of the nature of the flux.

MECHANICAL PROPERTIES

Plated or soldered contacts are often tested by measuring the force required to strip the bond at the interface between the two phases. Tensile strength tests were made on several specimens 1 cm² and 1.25 mm thick and provided with specially designed heavy caps. In Fig. 5(a) a sample is shown ready for test and in Fig. 5(b) the sample has been tested and shows the fractured silicon surfaces. The silicon broke in every case at a stress between 20 and 35 kg/cm² (3000 and 5000 lb/in.²). The break was always in the silicon about midway between the two contacts. In the sample shown, polycrystalline silicon was used. When monocrystalline material is used fewer cleavage planes appear.

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The Effect of Electron Traps on Electroluminescence

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ABSTRACT

Measurements of the temperature dependence of electroluminescent brightness and thermoluminescence of phosphor powder suspensions in Lucite and of single crystals demonstrate that electroluminescent brightness can be affected by electron traps. At low temperatures traps may, by field ionization, supply electrons in the region of high field. At higher temperatures they are thermally emptied, enhancing the field in the barrier region. Decreases in electroluminescent brightness occur in the temperature range where the role of traps is changing.

INTRODUCTION

In electroluminescent zinc sulfide phosphors shallow occupied electron traps or donors generate a region of high field by emptying to form an exhaustion layer. Deeper donors are field ionized to provide conduction electrons which are accelerated, in the region of high electric field, to velocities sufficient for impact excitation of activators (1). Comparison of the temperature dependence of electroluminescent brightness and of thermoluminescence suggests that in some temperature ranges traps have pronounced effects on electroluminescent brightness.

In order to determine the mechanism of the effect of traps on electroluminescent brightness, both powdered phosphors suspended in Lucite and single crystals have been studied in this work. Thermoluminescence and temperature dependence of brightness have been measured with photoluminescent and with electroluminescent excitation. The effect of frequency of the applied voltage on the brightness-temperature characteristics has also been determined.

EXPERIMENTAL

Measurements were made on powder samples of ZnS:Cu,Al suspended in Lucite, referred to hereafter as powder cells, and on single crystals of ZnS:Cu. Powdered phosphors were made by firing 60 g of ZnS with 0.7075 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 1.954 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ at 1100°C for $\frac{1}{2}$ hr in an atmosphere of 55 parts by volume of H_2S to 20 parts CO_2 , a moderately oxidizing condition.

Plastic suspensions were made by milling together the phosphor and Lucite in the volume ratio of 0.288 with a small amount of ethylene dichloride and then pressing this material out to a thickness of about 100 μ in a steam-heated press. The pressing operation was repeated several times to make electroluminescent sheets of uniform thickness and composition.

Activated single crystals were grown by sublimation in a small sealed-off quartz tube (2). The charge consisted of approximately 5 g of ZnS mixed with 5 mg of CuS which had been precipitated from a CuSO_4 solution.

Thermoluminescence and temperature dependence of brightness measurements on powdered samples were made with a previously described apparatus (3). The heating

rate for thermoluminescence was 5°C/min. Temperature dependence of brightness was determined point by point, allowing several minutes at each temperature before recording the brightness, in order to ensure steady-state conditions. A glass plate with conducting tin oxide coating held the electroluminescent layer against a metal disk which was in good thermal and electrical contact with the temperature-controlled block. A small amount of silicone oil was used on each side of the sample to eliminate air gaps at the electrodes. Electrical connections for electroluminescent excitation and dielectric constant and loss measurement were made to the temperature-controlled block and through an insulated thimble to the conducting glass coating. Most of the electroluminescent brightness measurements were made with 150 v rms applied to the sample.

For single crystals, a vacuum apparatus previously used for temperature dependence of conductivity (4) was provided with a window for excitation or observation. The crystal was pinched between platinum electrodes which were contained within a heavy-walled copper well. Electroluminescent brightness vs. temperature was determined with excitation by 200 v rms. The electrode separation was approximately 0.5 mm.

RESULTS AND DISCUSSION

Glow curves obtained on the phosphor powder before incorporation into the dielectric matrix are the same as that shown in Fig. 1 for a powder cell. The procedure of excitation with the G.E. B-H4 lamp (mainly 3650 Å radiation) substantially saturated the traps. With electroluminescent excitation at 400 v and 1000 cps, the glow curves were the same as for ultraviolet excitation except that the intensities were lower by factors ranging from 100 to 1000. As shown in Fig. 2, only the principal glow peak at 123°K is observable in the single crystals, and this only with 3650 Å excitation. Both from theory and from microscopic observations (5-7) of electroluminescent phosphors, it is believed that electroluminescent excitation is localized, thus accounting for the small number of traps filled during electroluminescent excitation.

In Fig. 3 are shown the photoluminescent and electroluminescent brightness of the powder cell, on which the data of Fig. 1 were obtained, as a function of temperature at several different frequencies of excitation. It is apparent

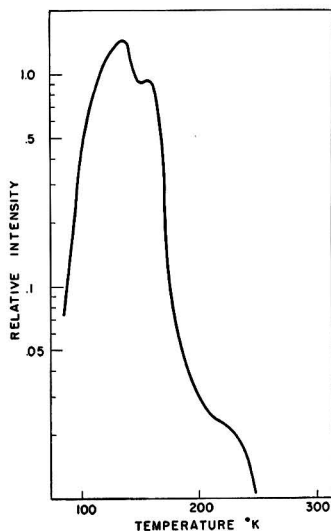


FIG. 1. Thermoluminescence of ZnS:Cu,Al powder

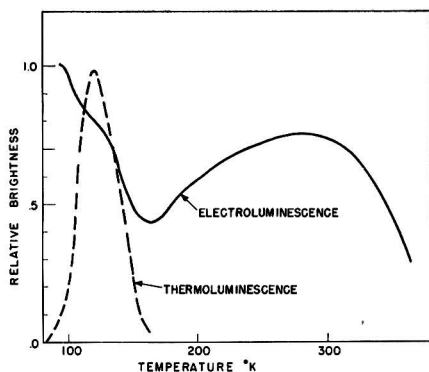


FIG. 2. Thermoluminescence and electroluminescent brightness of ZnS:Cu single crystal.

that the variations of electroluminescent brightness with temperature are peculiar to electroluminescent excitation rather than to the activator itself. The fact that similar behavior is observed in single crystals indicates that variations in brightness are not due to the characteristics of the dielectric. This view is substantiated by measurements of dielectric constant and loss of the phosphor suspensions and of pure Lucite. Pure Lucite shows a monotonic increase of dielectric constant and dielectric loss in going from 80° to 375°K, as do unexcited phosphor suspensions. However, there are pronounced maxima of dielectric loss near the temperatures of the glow peaks during thermoluminescence or at the temperature of the minimum in brightness during electroluminescent excitation of the powder cells.

It will be noted that the minimum in electroluminescent brightness occurs at a temperature a few degrees above the temperature of the principal glow peak. The structure in the temperature dependence of brightness shifts to

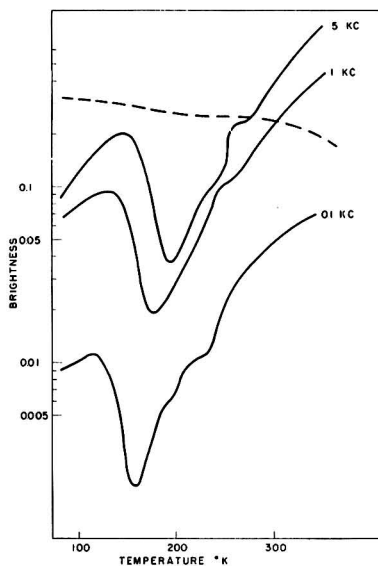


FIG. 3. Photoluminescent (dashed line) and electroluminescent brightness (solid lines) vs. temperature of ZnS:Cu,Al in Lucite.

higher temperatures with higher frequency of excitation. Changing the voltage of excitation over the range 120–300 v only shifts the characteristic temperature-brightness curve in brightness, not in temperature. The data are independent of the direction of temperature change and of the excitation history of the sample in contrast to the results of Gobrecht and co-workers (8) and of Neumark (9). In this work the sample attains a steady-state condition at the temperature of each measurement.

In this and other investigations (10) powder suspensions have been found in which the brightness drops off as the temperature is decreased and does not again rise at the lowest temperature measured, in contrast to the behavior of the samples reported here. The mechanism responsible for the temperature dependence of brightness should explain both types of behavior.

Electroluminescence is a field-dominated phenomenon. Large variations in brightness with temperature, therefore, may be expected if the electron traps responsible for thermoluminescence can in certain temperature ranges alter significantly the formation of the high-field region. The magnitude of the field, E , in the exhaustion layer increases with the number of shallow donors which can become thermally ionized during the half-voltage cycle. The localized states may be neutral when occupied, or may have a negative charge which is compensated by a nearby positive center, such as an ionized activator. In either case there will be an increase in the field in the exhaustion layer when an electron from the trapping state is removed from the barrier region. The density, N , of traps which ionize during the half-voltage cycle, τ , is

$$N = N_T(1 - e^{-k_1\tau}) \quad (1)$$

where N_T is the number of trapped electrons per unit volume and k_1 is the rate constant for thermal emptying

of traps and is given by $k_1 = s_1 e^{-\epsilon_1/kT}$. The quantities s_1 and ϵ_1 are the frequency factors for untrapping and trap depth, respectively. The average field \bar{E} resulting from the formation of an exhaustion barrier region with a concentration N of empty traps and N_d of empty donors is

$$\bar{E} = \left[\frac{2\pi e V_o}{\kappa} \right]^{1/2} (N + N_d)^{1/2} \quad (II)$$

where V_o is the magnitude of the applied voltage and κ is the dielectric constant of the phosphor. The exact expression for brightness depends on a detailed knowledge of all localized levels in the phosphor system. However, the following equation should describe to good approximation the dependence of the brightness on average field (1).

$$B_1 = A e^{-C/\bar{E}} \quad (III)$$

where A is a proportionality constant, and C is a constant characteristic of the material which depends on the efficiency of the excitation process and varies inversely with this efficiency. Substituting equation (I) and equation (II) in (III) the expression for the dependence of brightness on temperature resulting from the contribution of traps to the brightness by means of the exhaustion process is

$$B_1 = B_{10} \exp[-\beta e^{-k_1\tau}] \quad (IV)$$

The constants B_{10} and β result from combining constant terms of equations (I), (II), and (III). In order to obtain (IV) the approximation $N < N_d$ has been made. This approximate expression deviates from the more cumbersome, exact one only in the temperature range where the contribution of this term to the total brightness is quite small.

At low temperatures the traps may contribute to the electroluminescent output by being field ionized in the region of high field, thereby producing the electrons which are accelerated to impact excitation. The traps may provide the charge carriers for acceleration to the extent that they are not thermally ionized during the half-voltage cycle. This contribution to the brightness is given by

$$B_2 = B_{20} e^{-k_1\tau} \quad (V)$$

where B_{20} is temperature independent and is proportional to N and is also a function of the local field configuration. The total contribution to electroluminescent brightness from electron traps characterized by rate constant k_1 is

$$B = B_{10} \exp[-\beta e^{-k_1\tau}] + B_{20} e^{-k_1\tau} \quad (VI)$$

Differentiating (VI) with respect to temperature gives the following expression for the temperature, T_m , of the minimum

$$T_m = \frac{\epsilon_1}{k \ln(s_1\tau/\alpha)} \quad (VII)$$

where α is a constant given by

$$\alpha = \ln \left(\beta \ln \beta \frac{B_{20}}{B_{10}} \right)$$

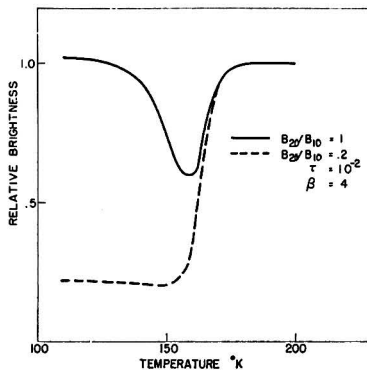


FIG. 4. Typical calculated electroluminescent brightness vs. temperature characteristics.

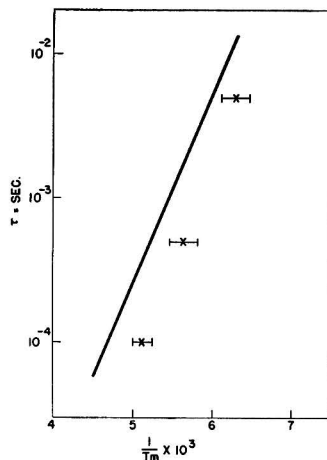


FIG. 5. Shift of electroluminescent brightness minimum with excitation frequency. Calculated: solid line; observed: points ($\beta = 4 B_{20}/B_{10} = 1$).

As seen on comparing Fig. 2 and 3 with Fig. 4, equation (VI) gives a temperature dependence of brightness in good agreement with experiment using values of $s_1 = 10^{10} \text{ sec}^{-1}$ and $\epsilon_1 = 0.25 \text{ eV}$ which are in accord with the thermoluminescence data. In addition, in Fig. 5, it is seen that by employing these same values in equation (VII) the position of the minimum agrees within 10% and its shift with frequency of excitation is in quantitative accord with the theory. There is evidence in the half-widths of both the thermoluminescence peak and the electroluminescent brightness minimum and in the temperature of the minimum for a considerable amount of retrapping and for the presence of more than a single trap depth. The small displacement of the calculated curve for the brightness minimum from the experimental points may be accounted for by the reduction of trap depth in regions of moderate field or by the uncertainty in frequency factor resulting from retrapping. Data of the type of Alfrey and Taylor are in accord with a low value of B_{20} as compared with B_{10} , Fig. 4, lower curve.

An alternative mechanism for the effect of electron traps on electroluminescent brightness requires a thermally

activated process governed by trapping for removal of electrons from ionized activators from the region of excitation. Removal from activators is followed by trapping in the bulk of the crystal. At low temperatures electrons cannot return to the activators, which results in a lower effective activator concentration and, therefore, lower efficiency. This mechanism results in the expression for brightness

$$B = B_0 \frac{[1 - e^{-k_1\tau}]}{[1 - e^{-(k_1+k_2)\tau}]} \quad (\text{VIII})$$

where k_2 and k_1 are the rates for removal from and return to the activators, respectively. Equation (VIII) is in accord with the data of Alfrey and Taylor. The return to high brightness at low temperature, characteristic of the authors' data, cannot be accounted for by equation (VIII) unless the system is permitted to relax completely during each cycle; such a relaxation process does not appear appropriate for the model. A similar difficulty arises when the effect of traps on mobility of conduction electrons is considered. A thermal contribution to the emptying of the deep donors responsible for electroluminescent excitation, suggested by Alfrey and Taylor (8), cannot result in a return of electroluminescent brightness to high values at low temperature and, thus, cannot account for the minimum in brightness reported here.

It is concluded that the effect of electron traps on electroluminescent brightness is largely the result of traps contributing to the exhaustion mechanism for high-field production at high temperatures and as sources of electrons for acceleration to impact excitation at low temperatures.

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Erosion of Steel by Hot Gases

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ABSTRACT

A vent-plug device for producing eroded surfaces on steel and other metals is described. Surfaces so treated have been shown by metallographic and x-ray analysis to duplicate structures encountered in many service applications. During the erosion of steel, as many as five distinct surface layers are produced. Retention of austenite in these eroded surfaces is an indication of the chemical alteration of the surface layers during erosion. The major portion of the investigation is concerned with a modified SAE 4330 steel. However, comparison experiments were made on Armco iron, and SAE 1015, 1040, and 1070 steels. The effect of carbon content on erosion behavior is illustrated by x-ray analysis.

INTRODUCTION

The interaction of a metal with high temperature, high pressure, and high velocity gases usually results in a significant deterioration of the surface, leading to a loss of material. This erosion is limited to surface deterioration by chemical alteration, which generally is the fundamental process. However, a complete description of erosion includes such possible simultaneous processes as me-

chanical abrasion, progressive stress damage, and surface fusion. In some applications, these processes may mask the effects of chemical alteration and control the erosion.

Erosion is a serious limitation in many applications where metals are exposed to gases at high temperatures. The bulk of prior observations (e.g., ordnance research) have been made on service-eroded material where an adequate knowledge of the conditions existing during

erosion is rare (1). To investigate the problem systematically it is necessary to simulate service-erosion conditions on a laboratory scale. One of the best ways to accomplish this is with a suitable vent-plug device. The various types of vent-plug devices which have been employed in previous research have two common features, namely: (a) an explosion source and chamber producing the high temperature, high pressure gases, and (b) a sample vent through which the explosion gases escape at high velocity.

In most of the previous vent-plug experiments, little or no attempt was made to insure actual service conditions in the vent-plug device. Consequently in general, erosion conditions were too severe to study adequately the effect of chemical alteration of the surface, i.e., surface fusion predominated (1). In addition, relatively few metallographic studies of vent-plug erosion have been made. However, concurrently with this research Dieter and Rink (2) studied the metallurgical aspects of vent-plug erosion of steel. Their results are pertinent to this report and will be discussed later. In addition to vent-plug experiments, considerable effort has been devoted to the study of service-eroded surfaces such as those of gun bores (3-11).

In the present work, conditions of erosion have been so adjusted that chemical alteration could be studied. By comparison of the surface layers of the vent-plug specimens with actual service-eroded material, it has been demonstrated that the surface structures are essentially identical.

EXPERIMENTAL

Vent-plug device.—Fig. 1 illustrates the vent-plug device which consists of a rifle receiver and action (A) coupled to an explosion block (B) by a section of rifle barrel. The explosion block is fitted for a knock-out plug (C) and a specimen and rupture-disk assembly (D). For comparison, a 30-06 caliber cartridge case (E) (length, 2.5 in.) is included. The important component of this device is the relatively long "L"-shaped gas path from the explosion source to the vent. In addition to baffling and cooling the gases, the "L" path provides a wad-catcher which prevents the rather heavy charge wadding from interfering with the gas passage through the vent. The total internal volume of the assembled device is about 15 cm³.

The specimen and rupture-disk assembly, based on a design by Evans, Horn, Shapiro, and Wagner (12) is shown

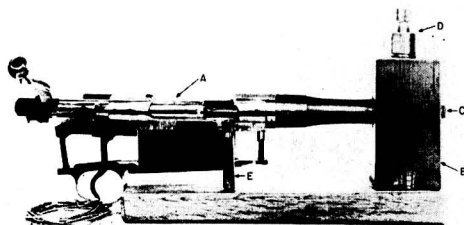


FIG. 1. Erosion vent plug device. A—Rifle receiver and action; B—explosion block; C—knock-out plug; D—specimen and rupture-disk assembly; E—30-06 caliber cartridge case (length—2.5 in.).

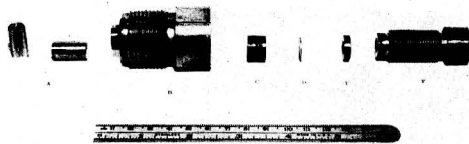


FIG. 2. Specimen and rupture-disk assembly. A—Vent-plug specimen; B—assembly body; C—choke; D—disk; E—retaining ring; F—retainer plug.

TABLE I. Nominal analysis of I.M.R. powder types 4064, 4320, and 4350 products of combustion

Component	% by Volume at room temperature	% by Volume at temperature of explosion
CO ₂	18.8	10.09
CO.....	46.4	45.35
H ₂	20.9	13.21
CH ₄	0.6	—
N ₂	13.3	11.00
H ₂ O.....	—	20.19
Metals as gas.....	—	0.16

in Fig. 2. The components are: assembly body (B), choke (C), disk (D), retaining ring (E), and retainer plug (F). A vent-plug specimen (A) is also included. One feature of this design is the location of the rupture disk on the exit side of the specimen vent. This insures maximum pressure build-up over the vent surface prior to the exhaust of the explosion gases. Rupture disks, with a circular unsupported area (0.25 in. in diameter) can be used to vary the bursting pressure over a wide range. In these experiments, 70-30 brass disks were employed. They were 0.020 in. thick and limited the bursting pressure to 16,000-18,000 psi. Pressures were determined by auxiliary crusher-gauge experiments. The choke diameter was fixed at 0.08 in. during these experiments, but it may be varied up to a diameter of 0.25 in.

The explosion charge was contained in a 30-06 cartridge case and was maintained in place with Duco cement. The entire charge of a Western "Super X" cartridge, loaded for a 220 grain projectile, was used. The powder in this commercial loading is single-base with a cylindrical grain. The average charge weight was 2.9106 g with a maximum weight difference between cartridges of about 0.04 g. This charge burns with an adiabatic flame temperature of about 2660°C and a maximum pressure potential of about 55,000 psi. Gas components produced during the explosion and their approximate proportions are listed in Table I (13).

Specimen materials and geometry.—Most of the vent plugs used in this investigation were machined from a modified SAE 4330 steel of the following composition: 0.34% C, 0.56% Mn, 0.21% Si, 0.017% P, 0.015% S, 2.6% Ni, 0.98% Cr, 0.15% V, and 0.24% Mo. Neither metallographic nor x-ray analysis showed the formation of an altered surface structure as a result of machining. The vents were rectangular in cross section and split longitudinally to give two specimens from each vent plug. The width and length of the vent were standardized at

0.30 and 0.75 in., respectively, while the thickness was varied to yield different surface areas. Unless otherwise specified, each sample was fired once.

The eroded surfaces were examined metallographically on a section cut at a fifteen degree taper to the surface. X-ray analysis was accomplished on a Norelco high-angle goniometer spectrometer with a chromium-target tube. Thermal treatments in purified hydrogen were also employed, in conjunction with metallographic and x-ray analysis, to investigate the specific character of individual layers. Weight-loss measurements were made on an analytical balance after the surface was carefully cleaned according to the following standardized procedure. Each half of a specimen was washed with water and soap. A nylon-bristle brush was used to insure complete removal of combustion products. Washing was continued for a period of 1 min. The specimen was then immersed in acetone, and finally blown dry in a filtered air blast.

In addition to the SAE 4330 vent plugs, 0.30 x 0.025 x 0.75 in.³ vent plugs were machined from Armco iron, and SAE 1015, 1040, and 1070 steels. To illustrate the effect of carbon content on erosion behavior, these specimens were eroded and the surfaces studied by x-ray and metallographic analysis.

RESULTS AND DISCUSSION

With a given set of explosion conditions in the vent-plug device (constant charge) and a specific material, the surface temperature of the specimen is a function of its vent surface area. Since erosion is sensitive to thermal input, i.e., cal/in.²/sec, it can be expected to vary with the vent surface area, which was conveniently altered by changing the vent thickness. The various layers produced during erosion generally have been described as chemically altered and thermally altered. The chemically altered layers, lying closest to the surface, undergo a significant compositional change as a result of chemical and thermal interaction with the explosion gases. However, the deeper thermally altered layers are not chemically changed except in the region closest to the overlying chemically altered layers. The thermally altered layers are differentiated from the base metal by microstructural changes.

A satisfactory nomenclature for the erosion layers is difficult to formulate. Because not all possible layers are always present in a given steel surface and because early erosion work generally did not detect chemically altered layers, some confusion exists in the literature. The fact that the metallographic appearance of the outer surface layers is radically altered leads to the inevitable conclusion that definite chemical changes have taken place. These layers are herein described (from the surface inward) as the outer white layer, the inner white layer, and the austenite-bearing layer. The designation of the "white" layers simply reflects their resistance to etching, which leaves them essentially as-polished in cross-section metallographic examination. The average total thickness of these layers ranges from 2×10^{-4} to 6×10^{-4} cm, and varies with the thermal input to the surface (vent surface area), the outer white layer being particularly sensitive in this respect. The thermally altered layers (commonly called "the white

layer" by the early investigators) are heated above the lower-critical temperature. They therefore undergo a structural alteration which leads to their delineation by differential etching. They consist of a thick layer heated above the upper-critical temperature and a relatively thin layer heated above the lower-critical temperature. These layers range in total thickness from 3.5×10^{-3} to 11.0×10^{-3} cm, being thicker the smaller the vent surface area. Under the conditions imposed, the thickness increased approximately linearly with decreasing vent surface area at a rate of about 0.0878 cm/in.² of surface area. Dieter and Rink (2) found that, with a fixed vent surface area, the depth of the thermally altered layers increased approximately linearly with adiabatic flame temperature of the charge. Both results reflect an increasing thickness with increasing thermal input to the surface (increasing severity of erosion conditions).

An interesting observation concerning the thermally altered layers is that almost complete structural homogenization is achieved during the first exposure. Only where segregation is pronounced, as in an annealed structure, is there any residual inhomogeneity after one exposure. Even in this extreme case, the remaining segregation is well toward the interior of the thermally altered layers. Thus, it appears that, after the initial exposure, there should be no effect of original microstructure on the chemical erosion behavior of the steel since the structure in the pertinent volume, close to the surface, is always the same. This qualitative observation is in agreement with the results of Dieter and Rink (2) who found no dependence of erosion weight loss on the original microstructure of a given steel.

Fig. 3 shows the layer configuration in the eroded surface of a 0.30 x 0.050 x 0.75 in.³ vent plug (surface area = 0.525 in.²). Two apparently chemically altered layers are noted—the outer and the inner white layers. A portion of the upper-critical, thermally altered layer is also shown. The x-ray spectrometer trace (Fig. 4A) indicates, in addition to the ferrite (110) peak, a weak austenite (111)

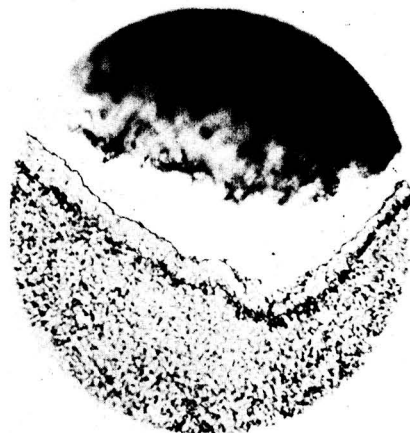


Fig. 3. Layer configuration in eroded surface of a 0.30 x 0.050 x 0.75 in.³ vent plug (Kalling's etch—1500 X) (15° taper section).

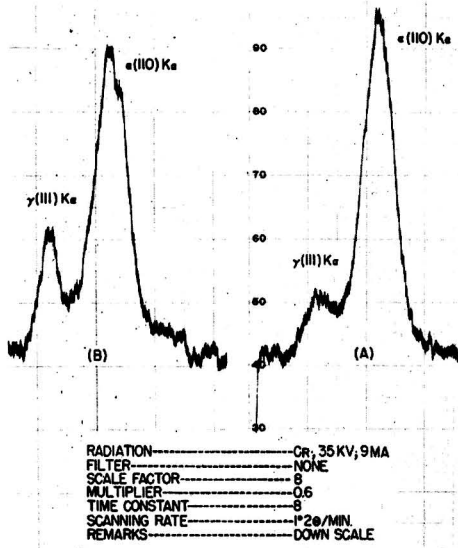


FIG. 4. X-ray spectrometer traces of eroded surfaces. A—0.030 x 0.050 x 0.75 in.³ vent plug; B—0.30 x 0.040 x 0.75 in.³ vent plug.

peak. The ferrite (110) peak intensity is considerably lower than that from the as-machined surface. This may mean that this diffraction is coming from the thermally altered layers. Some of the reduction in intensity may be attributed to residual stress and some to the absorption effect of the overlying chemically altered layers. Heat treatments in purified hydrogen, designed to decompose the retained austenite, produced no simultaneous metallographic alteration of the outer or inner white layers. Therefore, it was concluded that these layers did not contain the retained austenite. The relatively small amount revealed by x-ray analysis is apparently not sufficient to produce a recognizable indication of the austenite-bearing layer in a metallographic cross section of this narrow region.

Fig. 5 is the metallographic section of a 0.30 x 0.040 x 0.75 in.³ vent plug (surface area = 0.510 in.²). In addition to the outer and inner white layers, a third chemically altered layer is present in this specimen. Fig. 4B shows the x-ray spectrometer trace from the surface of this specimen. Note the increase in the austenite (111) peak intensity and the decrease in the ferrite (110) peak intensity in comparison to Fig. 4A. The specific character of the additional layer in this specimen was indicated by the heat treatments described above, in which the thermal decomposition of the retained austenite (verified by x-ray analysis) led to the metallographic change illustrated in Fig. 6 (14). This layer is, therefore, designated as the austenite-bearing layer.

As the vent surface area was further reduced to 0.472 in.² by reducing the vent cross section, there was no appreciable change in the layer configuration. The only change noted was in layer thicknesses. The x-ray data indicate an increasing proportion of austenite in the

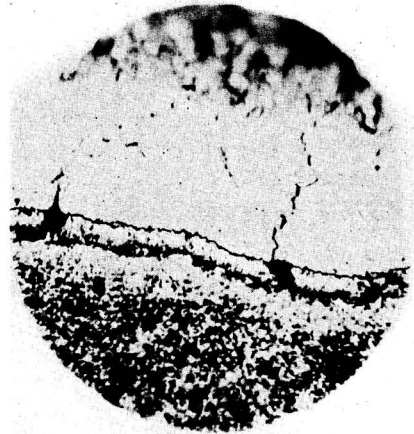


FIG. 5. Layer configuration in eroded surface of a 0.30 x 0.040 x 0.75 in.³ vent plug (Kalling's etch—1500 X) (15° taper section).

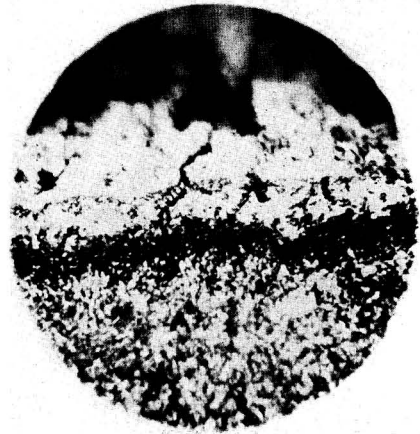


FIG. 6. Layer configuration in eroded surface of a 0.30 x 0.025 x 0.75 in.³ vent plug after thermal treatment at 1200°F for 2 min (Kalling's etch—1500 X) (15° taper section).

irradiated volume with decreasing vent surface area. To illustrate this tendency, the ratio of the integrated intensity of the austenite (111) line to that of the ferrite (110) line (I_{γ}/I_{α}), as a function of vent surface area, is shown in Fig. 7. Integrated instead of peak intensities were used to take into account the effect of residual stress on the peak intensity of the ferrite (110) line.

Table II lists observed x-ray parameter data for various materials in vent-plug surfaces. The lattice parameter of the retained austenite was quite constant even after several exposures of a given vent plug. The maximum variation in parameter was about $\pm 3 \times 10^{-3} \text{ \AA}$ in repeated experiments up to twelve exposures. This indicates that the austenitizing element, which could be carbon or nitrogen, singly or in combination, is absorbed to saturation in the retained phase. Although quantitative figures are impossible on the basis of this research (since the

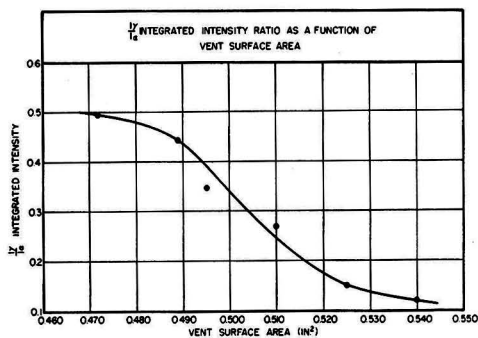


FIG. 7. Variation of the integrated-intensity ratio $I_{\gamma(111)}/I_{\alpha(110)}$ as a function of vent surface area.

TABLE II. Lattice constants of materials in vent-plug surfaces

Peak identification	Bragg angle (Degrees 2θ)	"d" (Å)	Lattice parameter (Å)	Remarks
Ferrite (110)	68.40	2.038	2.882	Ferrite in the as-machined surface
Ferrite (110)	68.24	2.042	2.888	Ferrite in the eroded surface
Austenite (111)	66.00	2.103	3.643	In eroded surface
Martensite (110)	68.45	2.037	$A_0 = 2.880$	In eroded surface after a number of exposures
Martensite (101)	68.10	2.046	$C_0 = 2.906$ ($C/A = 1.009$)	

exact effect of the alloy elements and possibly oxygen from the explosion gases is unknown), it is probable that the observed parameter involves a concentration of about 1.7 wt % carbon or about 2.0 wt % nitrogen (15, 16). These estimates are based on an oversimplified picture of single-element interaction. Speculating further, a consideration of the Fe-C (17) and Fe-N (16) phase diagrams indicates that carbon may be the major austenitizing element under the imposed conditions. If the hypothesis that the active austenitizing element is absorbed to saturation is correct, the low temperature (about 775°C) associated with saturated nitrogen-austenite at 2.0 wt % nitrogen eliminates it as the active element. This follows from the fact that the relatively thick thermally altered layers (heated above about 720°C) preclude this low temperature in the austenite-bearing layer which is much closer to the surface. Following Feurstein and Smith (18), and Dieter and Rink (2), it is clearly meaningless to discuss thermal levels in eroded surfaces on the basis of equilibrium diagrams. Dieter and Rink (2) show that the rate of heating which obtains in eroded vent-plug surfaces (10°F/sec) can cause an increase in the lower critical temperature of at least 500°F. However, this should not affect the general conclusions derived from observations of the equilibrium diagrams.

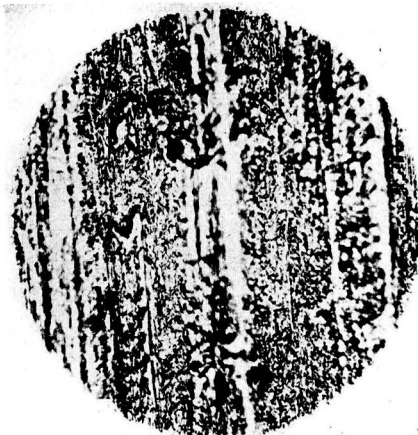


FIG. 8. Surface of as-machined vent plug (unetched—1500 X).

Dieter and Rink (2) also investigated the relative amounts of retained austenite formed by various explosion gases. Explosions of N_2O-H_2 and of $CO-O_2$ gas mixtures gave about the same relative amounts of retained austenite. Explosions of H_2-O_2 gas mixtures, although free of carbon and nitrogen, produced smaller but significant amounts of retained austenite. This last result apparently indicates that the enrichment of the retained austenite zone is not entirely due to interaction with the explosion gases. Therefore, internal segregation due to the steep thermal gradient from the surface inward may generally account for a small part of the retained austenite.

After a number of exposures of a given vent, the ferrite (110) line tends to dissociate into a doublet, indicating tetragonal martensite in the thermally altered layers. The doublet is resolvable after two or three exposures with a $0.30 \times 0.025 \times 0.75$ in.³ vent plug. The lattice constants for this martensite are given in Table II. On the basis of the above discussion, carbon is assumed to be the major contributor to the tetragonality, and the martensite probably contains approximately 0.43 wt %. The fact that the solute content required for the martensite observation is less than that required for the austenite observation is consistent with the position of the retained austenite closer to the vent surface than the martensite.

The precise nature of the outer and inner white layers was not determined in this investigation. Deep etching failed to develop any structure in either of the layers, and both appeared to be generally unattacked by standard etching reagents. The inner white layer seems less resistant to erosion than either the outer white layer or the austenite-bearing layer. This is illustrated in Fig. 5 where pocket-type erosion at the base of cracks extending through the outer white layer is evident.

That chemical interaction occurs without appreciable surface fusion is indicated by Fig. 8, 9, and 10. Fig. 8 shows the as-machined surface, while Fig. 9 is a photomicrograph of the surface of a $0.30 \times 0.050 \times 0.75$ in.³ vent plug which was fired once. A comparison with Fig. 3 shows that chemical interaction took place even though

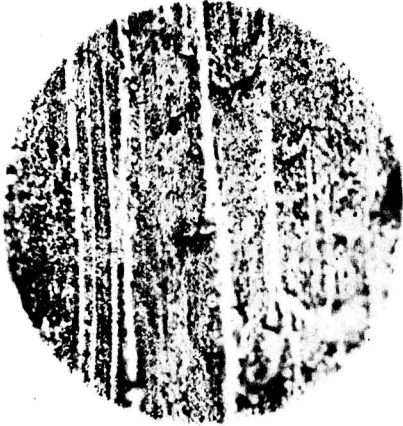


FIG. 9. Surface of eroded, $0.30 \times 0.050 \times 0.75$ in.³ vent plug (unetched—1500 \times).



FIG. 11. Surface of heavily-eroded $0.30 \times 0.025 \times 0.75$ in.³ vent plug—after 12 exposures (unetched—1500 \times).

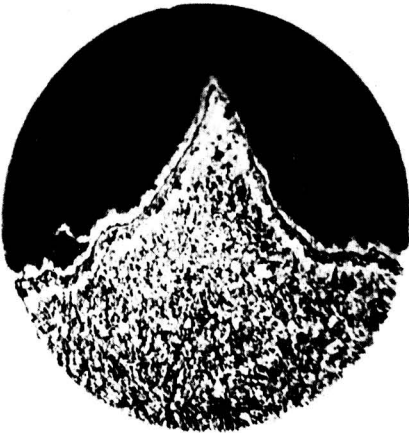


FIG. 10. Layer configuration in eroded surface of a $0.30 \times 0.040 \times 0.75$ in.³ vent plug—near exit end (Kalling's etch—1500 \times) (15° taper section).



FIG. 12. Layer configuration in heavily eroded $0.30 \times 0.025 \times 0.75$ in.³ vent plug showing chemical alteration penetrating along crack (Kalling's etch—1500 \times) (15° taper section).

the surface appears essentially unchanged by firing. Actually the rather sharp machining marks which are out of focus in the photomicrographs did not suffer resolvable change as a result of this exposure. It is expected that fusion would be most evident at these projections and would result in pronounced smoothing. Fig. 10 illustrates the appearance of such a projection on taper section. Further evidence against appreciable surface fusion, i.e., fusion of outer white layer material, is given in Fig. 5. The existence of pocket-type erosion at the base of cracks in the outer white layer indicates the rigidity of this material during erosion. As the vent surface area was reduced, the machining marks were gradually leveled by erosion. Complete leveling occurred first near the entrance end of the vent. However, no obvious signs of general surface fusion were noted after one exposure, although it is entirely possible that fusion did occur at the immediate

entrance end. Fig. 11 shows the surface of a $0.30 \times 0.025 \times 0.75$ in.³ vent plug which was fired twelve times. The obvious wash pattern indicates general fusion.

Microcracking was often seen in the vent-plug surfaces after erosion. Cracks had their origin either in the outer white layer or appeared to radiate from inclusions in the thermally altered layer. These cracks result from thermal shock and volume changes during transformation which are experienced by the hot surface layers as they are quenched by the surrounding mass of the vent-plug device. Unlike many examples of service erosion, cracking does not appear to play an important role in this vent-plug erosion. Penetration of the chemically altered layers into the first thermally altered layer was, however, noted to occur along cracks which were open to the explosion gases. Fig. 12 illustrates this process in a $0.30 \times 0.025 \times 0.75$ in.³ vent plug fired six times.

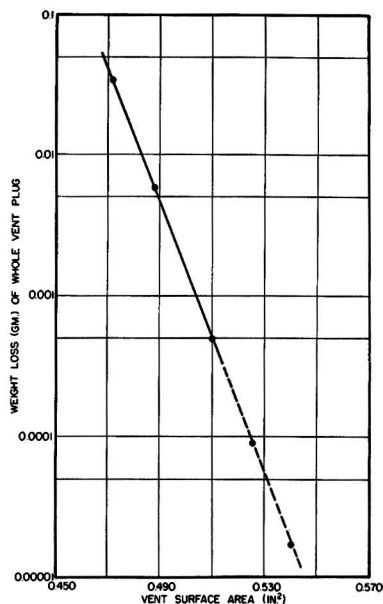


FIG. 13. Weight loss due to erosion as a function of the vent surface area.

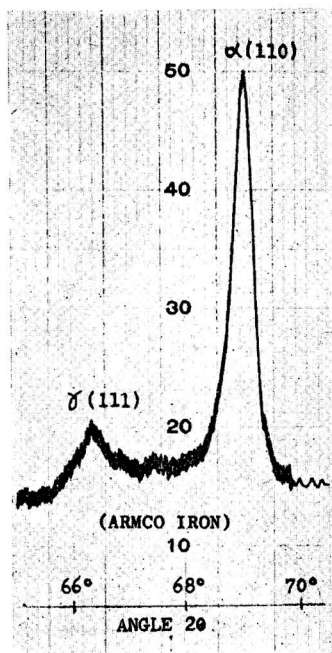


FIG. 14. X-ray spectrometer trace from eroded surface of $0.30 \times 0.020 \times 0.75$ in.³ Armeo-iron vent plug. Radiation, Cr, 35 kv, 9 ma; filter, none; scale factor, 16; multiplier, 0.6; time constant, 8; scanning rate, $1^\circ 2\theta/\text{min}$; remarks, downscale.

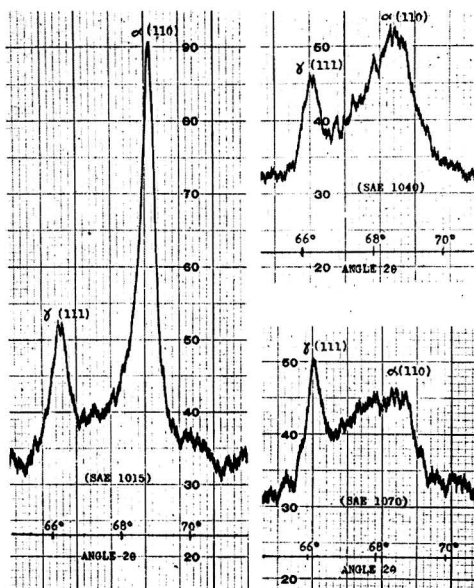


FIG. 15. X-ray spectrometer traces from eroded surfaces of $0.30 \times 0.025 \times 0.75$ in.³ vent plugs made from S.A.E. 1015, 1040, and 1070 steels. Radiation, Cr, 35 kv, 9 ma; filter, none; scale factor, 8; multiplier, 0.6; time constant, 8; scanning rate, $1^\circ 2\theta/\text{min}$; remarks, downscale.

As was mentioned previously, the effects of erosion under a given set of conditions can be expected to vary with the vent surface area. Therefore, the loss of surface material due to erosion should vary with the vent surface area. The smaller the area the greater should be the weight loss. Fig. 13 illustrates this behavior. The logarithm of the weight loss under the imposed conditions is seen to be a linear function of the vent surface area.

As a comparison experiment, Armeo iron, and SAE 1015, 1040, and 1070 steels were eroded. All specimens were $0.30 \times 0.025 \times 0.75$ in.³ vent plugs and were fired once. X-ray spectrometer traces of the eroded surfaces are shown in Fig. 14 and 15. It is evident that as the carbon content of the base steel increases, the greater is the quantity of retained austenite and the more strained is the ferrite or martensite, as the situation may be. Note that even in Armeo iron some retained austenite is produced in the eroded surface by this short exposure. Layered surface structures similar to those developed on SAE 4330 vent plugs also appeared on these specimens.

CONCLUSIONS

1. The process of chemical erosion may be conveniently studied with a vent-plug device in which suitable cooling of the explosion gases prevents surface fusion.

2. It appears that significant erosion can occur by the interaction of high temperature, high pressure, and high velocity gases without the expedients of appreciable surface fusion and mechanical factors.

3. The eroded surfaces produced under these conditions consist of various chemically and thermally altered layers.

4. Austenite, retained in the surface (neglecting small amount apparently due to internal segregation), is a product of erosion and indicative of chemical alteration. The relative amount of retained austenite varies with the exposure, being greater the more severe the conditions, in this case, the smaller the vent surface area.

5. Both nitrogen and carbon derived from the explosion gases could cause the retention of austenite. On the basis of lattice parameter measurements, it appears that carbon is probably more active than nitrogen in this respect.

6. The original carbon content of the steel has a pronounced effect on the character of the eroded surface as studied by x-ray analysis. The greater the original carbon content, the greater the quantity of retained austenite in the surface and the more strained is the ferrite or martensite in the thermally altered layers.

7. Metallographic observations of the thermally altered layers indicate that there should be virtually no dependence of erosion behavior on the original microstructure of the steel.

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Sodium-Aluminum Equilibria in Cryolite-Alumina Melts

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ABSTRACT

A qualitative and quantitative study of sodium-aluminum equilibria in cryolite-alumina melts was undertaken to shed more light on the cathode reactions in the aluminum cell. Measurements were made in alumina crucibles from 940° to 1010°C. Lead was used as an auxiliary sodium "sink." Results show that, while aluminum is more noble than sodium, their deposition potentials are not far apart (of the order of 0.1-0.2 v), and that, under the nonequilibrium conditions existing in an industrial cell, some sodium may be codeposited with aluminum at the cathode.

INTRODUCTION

Although aluminum has been produced commercially by electrolysis for over sixty years, much basic knowledge of the reduction process is still missing. This lack of information is largely due to such experimental difficulties as:

1. The lack of materials of construction which are completely resistant to the action of molten cryolite and aluminum around 950°-1000°C. Even carbon or graphite is not inert in the presence of aluminum and fused fluorides.

Practically all metals alloy with molten aluminum, and most nonmetallic refractories dissolve in fused fluorides to some extent.

2. Room temperature studies of solidified melts are often meaningless; major changes in melt structure may take place on going from the liquid to the solid state. Furthermore, certain chemical states which exist at high temperatures are unstable at room temperature and vice versa.

In view of these problems and others, it is not surprising

that several theories have been proposed to explain the cathodic processes in the aluminum cell.

Present Status of Aluminum Reduction Theories

Various theories pertaining to the electrolytic production of aluminum have been summarized recently (1, 2).

Most investigators attribute the Faraday inefficiency at the cathode of aluminum cells to the formation of metallic sodium. There are three main groups:

(A). The "primary sodium" school of thought, which maintains that sodium is produced at the cathode by direct electrochemical reduction and then displaces aluminum from the melt chemically (3-6).

(B). The Grünert group (7), which states that sodium is more noble than aluminum and that kinetic factors account for the fact that the major cathodic product is aluminum.

(C). The "primary aluminum" school, which believes that aluminum metal comes from the direct electrochemical reduction of an aluminum donor from the melt (1, 2, 8-12).

In recent years, it has been recognized that monovalent aluminum compounds may constitute another important source of current inefficiency in aluminum cells (9, 11). Such monovalent aluminum compounds can result from incomplete cathodic reduction or from chemical interaction between aluminum metal and trivalent aluminum compounds; they can then be reoxidized at the anode.

There is also a possibility that carbide formation at the carbon cathode may account for some current inefficiency. Aluminum carbide Al_4C_3 is commonly observed in the lining of cells which have been removed from service. It has been shown (13) that this compound can be formed electrochemically. It is also possible that sodium carbide Na_2C_2 may play a part in cathode reactions. This compound has been reported on several occasions (14-16). From the meager data available, Na_2C_2 appears to be a gas at cell temperatures. Its sublimation temperature is lower than the boiling point of sodium and its stability range is not definite. Altogether, Piontelli (10) feels that carbide reactions are important only during the early stages of operation of a cell.

The object of the present work is to provide additional data for evaluation of the various theories of cathode reactions in the aluminum cell.

Preliminary Experiments

It was decided to study first the spontaneous reactions of aluminum and sodium with cryolite melts. If a reaction between sodium or aluminum and a melt can take place spontaneously, then it can certainly occur when these elements are produced by electrolysis from this same melt, physical conditions being identical. Therefore, a study of the spontaneous reactions between aluminum or sodium and cryolite-alumina baths should shed some light on the phenomena taking place during electrolysis.

Grjotheim (9) passed sodium vapors through powdered cryolite at 900°C and detected aluminum globules after the experiments. Therefore, under these conditions, sodium is less noble than aluminum.

Unfortunately, Grjotheim's conditions differ from those existing in a reduction cell in several important respects:

1. Cell operating temperatures are of the order of 970°C, or well above the boiling point of sodium. Consequently, if any sodium exists in a cell, it cannot be present at a partial pressure much above 1 atm. Accordingly, the activity of sodium in an industrial cell may be widely different from that in Grjotheim's experiments. This point is amplified further below.

2. The equilibrium constant may change between 900° and 970°C.

3. Reactions in solid baths may differ from those in molten salts.

Grube and Hantelmann (17) also reacted pure sodium with cryolite-base melts at 1000°-1020°C. They found that aluminum was displaced by sodium from $NaF \cdot AlF_3$ melts. Although sodium is above its boiling point at 1000°C and vaporizes rapidly, the contact time between liquid Na and melt appeared to be sufficiently long to displace aluminum.

To come closer to industrial cell conditions, a series of reactions between cryolite-base melts and sodium were run at usual cell temperatures and above. Since pure liquid sodium cannot exist at these temperatures at atmospheric pressure, sodium-lead alloys were used to supply the necessary Na at a partial pressure of 1 atm. This was achieved by heating, at atmospheric pressure, Na-Pb alloys containing excess Na to the temperature at which the reaction between sodium and melt was to be carried out. Aluminum is only slightly soluble in molten lead and sodium is almost insoluble in aluminum; as a result, any appreciable amount of aluminum formed by reaction between Na-Pb alloys and cryolite-base melts comes out as a distinct phase of nearly pure aluminum.

Na-Pb alloy was reacted in graphite crucibles with the following melts: (a) pure cryolite at 1010°C; (b) 92% cryolite, 8% calcium fluoride at 975°C; (c) 88% cryolite, 4% alumina, 8% calcium fluoride at 975°C.

In all cases the charge was melted first, then the alloy was dropped into the melt. Reaction times were of the order of 15-30 min, after which the melts were cooled. In all cases a number of small globules of aluminum were found floating on top of the lead alloy layer as a distinct phase.

These experiments prove that, in pure cryolite as well as in reduction baths, sodium at 1 atm partial pressure displaces aluminum spontaneously. They show that sodium is less noble than aluminum under reduction pot operating conditions, and thus disprove Grünert's theory (7). They do not necessarily eliminate the possibility that, during electrolysis, a certain amount of sodium may be codeposited at the cathode with aluminum.

To obtain additional information on the latter point, a quantitative study of sodium-aluminum equilibria was undertaken.

Theoretical Considerations

Experience and previous work (18) indicate that some sodium is always present when aluminum is in contact with cryolite-base melts. The equilibrium amount of sodium in such a system is very small for the following reasons.

1. The solubility of sodium in aluminum is very low

(0.01–0.1 at. %). Since the reactions take place above the boiling point of sodium, no separate liquid sodium phase exists in the reaction mixture.

2. Sodium at 1 atm partial pressure produces aluminum in the presence of cryolite-base melts. Therefore, the equilibrium vapor pressure of sodium must be less than 1 atm, and its concentration in molten aluminum must be below its solubility limit.

The concentration of sodium in aluminum metal is so low that usual analytical methods are not sufficiently accurate. To overcome this difficulty lead was used as an auxiliary sodium "sink," and the concentration of sodium was determined in the lead phase rather than in the aluminum phase. From this, the sodium activity can be obtained (19).

As stated above, the mutual solubilities of lead and aluminum are small [Pb in Al, 1.8 at. %; Al in Pb, 10 or less at. % at 970°C (20)] and the solubility of sodium in lead is high. Therefore, at 940°–1010°C there are two phases, i.e., a phase rich in aluminum containing small amounts of lead and sodium, and a lead-rich phase containing most of the sodium and a little aluminum. Accordingly, it was assumed that the activity of aluminum in the aluminum-rich layer is essentially unity, and that neither the activity nor the concentration of sodium in the lead layer is significantly altered by the amount of aluminum in that layer.

An aluminum cell, under normal conditions, does not operate reversibly. The cathode polarization can cause a build-up of sodium in aluminum in excess of the equilibrium activity a_e . As the overvoltage gradually increases, the sodium at the cathode eventually reaches a level corresponding to a partial pressure of 1 atm and, from that point on, sodium will be evolved continuously.

The activity of sodium in aluminum or lead corresponds, at any temperature, to a definite sodium fugacity and approximately to the sodium vapor pressure p . If p^0 is the vapor pressure of pure sodium at that temperature, the relation is $a \approx p/p^0$.

The sodium activity at 1 atm partial pressure, a_L , becomes

$$a_L = 1/p^0 \quad (I)$$

if p^0 is in atmospheres.

Any further increase in the cathode potential only increases the rate of evolution of sodium gas, but cannot raise the activity above a_L .

At the cathode potential required to deposit aluminum reversibly, the sodium activity has its equilibrium value a_e . To calculate the extra voltage required to evolve sodium at 1 atm.

$$E_L = \frac{RT}{nF} \ln \frac{a_L}{a_e} \quad (II)$$

or, in the case of sodium,

$$E_L = 1.984 \times 10^{-4} T \log \frac{a_L}{a_e} \quad (III)$$

E_L is the difference between the reversible deposition potential of aluminum and that of sodium at 1 atm partial pressure of sodium vapor.

Previous Work

The sodium-aluminum equilibrium in fluoride melts has been studied by Jander and Hermann (18). They reacted aluminum with NaF-AlF₃ melts at 1090°C and determined the concentration of sodium in the aluminum metal and of total aluminum compounds in the melt. Alumina containers were used to run the reactions. No attempt was made to correct for the difference between concentrations and activities, and equilibrium constants were calculated on the basis of concentrations. Accuracy of the results was further limited by the small concentrations of sodium which had to be analyzed.

Grube and Hantelmann (17) determined the melt composition at which aluminum is in equilibrium with sodium at 1000°–1020°C as being about 6% AlF₃–94% NaF, whether or not alumina was present. Since elemental sodium was introduced into the reaction mixture and was vaporizing rapidly, there is some question as to whether true equilibrium was attained.

The use of lead as an auxiliary sodium "sink" has been mentioned by several workers in the field of aluminum research. Pearson and Waddington (21) tried to extract "metal fogs" with lead, and found evidence of sodium in the lead. Andrieux and Bonnier (22) ran short-term laboratory electrolyses with lead cathodes. Fischer (23) ran an industrial aluminum cell with a lead cathode for many months. It is important to note that none of these experiments represents reversible equilibrium conditions.

EXPERIMENTAL

The determination of the equilibrium activity of sodium in lead, in the presence of aluminum and cryolite melts, consisted of: (a) determination of the equilibrium concentration of sodium in lead after reaction; and (b) measurement of the activity of sodium in lead at various concentrations and temperatures in a separate study (19).

The general procedure consisted of reacting a cryolite melt, aluminum, and lead or a sodium-lead alloy in a covered container for varying periods of time. The reaction furnace was open to air and the container was not wholly airtight. At the end of each run, the container was chilled and samples taken for analysis.

The choice of container material was critical. Graphite crucibles were used at first, but were unsuitable for quantitative studies. Both sodium and aluminum react with carbon at the temperatures at which the experiments were performed. As a result, sodium is removed at the crucible walls, so that a true equilibrium can never be attained; instead, a steady state is reached where sodium is removed by the graphite at the same rate as it is driven into the lead layer. This steady state is dependent upon container geometry and, consequently, has no thermodynamic significance.

Grube and Hantelmann (17) also found that graphite crucibles were not suitable and used BeO crucibles instead. Since the solubility of BeO in cryolite is 8% by weight (24), some of this material dissolves; also, since the rate of dissolution is slow, the amount of BeO in the cryolite melt varies with the reaction time. This introduces a component into the melt whose effect is unknown.

Alumina was the only other available material that would not introduce a new component into the reaction mixture. However, use of this material automatically restricted these experiments to melts saturated with alumina. When carrying out experiments in alumina containers, powdered Al_2O_3 was added to cryolite in a quantity sufficient to attain saturation.

Vitrified alumina crucibles (Remmey 99AV) were used, with cover plates cut from Monofrax MH fused-cast alumina (Carborundum Co.). The cover was drilled to allow insertion of a stirrer. Since carbon could not be tolerated, the stirrer was fabricated by inserting a sealed piece of inconel tubing part way into a piece of dense alumina tube, so that inconel was in contact with melt but not with any liquid metal. A thermocouple was inserted inside the inconel tubing for temperature measurement. The maximum life of these stirrers was 4-5 hr. No absolutely leakproof all-alumina thermocouple protection tubes were available for the above use.

Equilibrium was approached from the low-sodium side, by using sodium-free lead plus aluminum, and from the high-sodium side by using sodium-rich lead plus aluminum. In the latter case the extra aluminum was added solely to maintain a homogeneous system, by providing an aluminum reservoir for side reactions.

Raw materials were natural cryolite (commercial), alumina (Kaiser, reduction grade), AlF_3 (Aleo X-2A), NaF (reagent), lead (C.P.), aluminum (99.99%), and sodium (reagent).

TABLE I. Sodium-aluminum equilibria

Equilibrium concentration of Na in Pb, in the presence of Al metal and cryolite melt saturated with Al_2O_3 . No carbon present.

Initial metal phases	Temp, °C	Na in Pb % by wt	NaF:AlF ₃ final wt ratio
Al + Na-Pb	1010	5.78	1.50
Al + Na-Pb	1010	5.87	1.42
Al + Na-Pb	1010	6.05	1.89
		5.90avg	
Al + Na-Pb	970	5.63	1.67
Al + Na-Pb	970	5.06	1.60
Al + Na-Pb	970	6.46	1.71
Al + Na-Pb	970	5.02	1.66
		5.54avg	
Al + Pb	970	3.80	1.54
Al + Pb	970	3.89	1.58
Al + Pb	970	4.26	1.60
Al + Pb	970	3.98	1.60
		3.98avg	
Al + Na-Pb	940*	5.08	1.65
Al + Na-Pb	940	5.81	1.54
		5.44avg	

* Phillips, Singleton, and Hollingshead (25) report that the freezing point of the cryolite-alumina eutectic is 962°C. The fact that the melt was still liquid at 940°C in the present equilibrium investigations may have been due to supercooling, or excess NaF, or both.

Reaction time was varied from about 30 min to 6 hr. Jander and Hermann (18) state that 1 hr appears to be sufficient for reaching equilibrium. However, in the present work, attainment of equilibrium appeared to require a somewhat longer period of time (approx. 2 hr) because of the additional lead phase in the system. In order to help reach equilibrium as quickly as possible, intermittent stirring was used.

Temperature varied from 940° to 1010°C. At the end of each run, the container was removed from the furnace and placed on a graphite plate for rapid chilling, to avoid possible composition changes during cooling.

Once cold, the container was cracked. The metal slug was cleaned to remove any melt, and the aluminum part was separated from the lead layer. The latter was then sampled for sodium analysis, which was carried out with a Beckman DU spectrophotometer with flame photometer attachment.

The NaF:AlF₃ ratio of the melt after reaction was checked by pyrotitration.¹

During the course of an experiment, the NaF:AlF₃ ratio changed. When starting with a sodium-rich lead alloy, aluminum is displaced from the melt and replaced by sodium ions so that the ratio increases. Conversely, when starting with sodium-free lead and aluminum the ratio decreases. It was generally attempted to achieve a final ratio of 1.50 by adjusting the initial melt composition. However, because of the empirical nature of this correction, some variation in final NaF:AlF₃ ratio occurred, as shown in Table I.

RESULTS

The results of sodium-aluminum equilibrium determinations are presented in Table I.

At 970°C, the final Na content of the lead in an initially Na-free Pb is consistently lower than in an initially Na-rich Pb alloy. This gives a range within which the true equilibrium value must lie, and also shows the experimental limitations of the method used. Better reproducibility and better definition of the limits within which the equilibrium lies probably could be achieved by working in an inert atmosphere.

The data from Table I were used to calculate E_L [equation (II)]. The equilibrium activities of sodium in lead were determined from the corresponding concentrations (19). Values of p^0 for sodium used to calculate a_L were obtained from the following expression

$$\log P_{(nm)} = -5567/T - 0.5 \log T + 9.235 \quad (26) \quad (IV)$$

These results are given in Table II.

DISCUSSION

Table II shows that the values of E_L are quite small. It requires only 0.1 to 0.2 v above the thermodynamic deposition potential of aluminum to start producing the

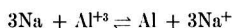
¹ Cryolite corresponding to a balanced formula Na_2AlF_6 has a NaF:AlF₃ weight ratio of 1.50 and is neutral to phenolphthalein, while for NaF:AlF₃ > 1.50 it is alkaline. Pyrotitration consists in adjusting an unknown melt composition with known amounts of reagents until the neutral point is reached and then calculating the unknown composition.

TABLE II. Results

Temp, °C	1010	970	970	940
Initial metal phases in equilibrium runs	Al + Na-Pb	Al + Na-Pb	Al + Pb	Al + Na-Pb
Equilibrium % Na in Pb by wt (avg)	5.90	5.54	3.98	5.44
Equilibrium mole fraction N (Na in Pb)	0.360	0.345	0.272	0.342
Equilibrium activity of Na in Pb (a_e)	0.17	0.12	0.068	0.10
a_L	0.347	0.461	0.461	0.582
E_L (in mv)	79	143	205	184

first traces of sodium at 1 atm pressure, under which conditions it can be given off continuously from the cathode. This small difference in deposition potentials explains why, until recently, the controversy between the proponents of primary aluminum deposition and primary sodium deposition has remained unresolved.

From a quantitative standpoint the results are valid only in melts saturated with Al_2O_3 . Qualitatively, however, it was shown earlier that aluminum is more noble than sodium in melts ranging from pure cryolite to cryolite saturated with alumina, i.e., E_L must have the same sign in all these melts. From mass-action considerations, it would be expected that Al_2O_3 would shift the reaction



to the right (in this equation Al^{+3} represents any aluminum donor, not necessarily Al^{+++} ions). Consequently, it is reasonable to believe that, at lower alumina concentrations, sodium activity would be somewhat higher and the value of E_L somewhat smaller than in cryolite melts saturated with alumina. However, since E_L is already small in Al_2O_3 -saturated melts, it cannot be much smaller in ordinary reduction bath. In this connection the studies of Grube and Hantelmann (17) showed that the presence of alumina did not affect the reactions between sodium or aluminum and AlF_3 -NaF melts. Experimental verification of this point must await the development of an inert container material.

Mass-action considerations would also predict that, when the NaF:AlF₃ ratio increases, the Na activity in lead or aluminum increases likewise. The present work was not intended to investigate the ratio effect and, within the narrow limits of NaF:AlF₃ ratio covered by these data, no significant trend is apparent. Again, the necessity of working in saturated alumina solutions limits the possibility of investigating the effect of ratio, since, at a fixed temperature, the alumina solubility varies as the ratio changes; thus, the effect of more than one variable would come into play.

Table II brings out the effect of temperature on E_L . Even though the equilibrium concentration of sodium may not greatly change between 940° and 1010°C, the equilibrium activity increases at higher temperatures, while the limiting activity decreases at the same time. As a result, E_L decreases by almost 100 mv between 940° and 1010°C.

The data show a small but definite range of cathode potential in which aluminum can be produced electrolytically, but in which sodium cannot be evolved at a partial pressure of 1 atm. The lower limit of this range is the reversible deposition potential of aluminum, and its span

is E_L . In this range, the sodium activity at the cathode must lie between a_e and a_L . If the cathode potential is raised to the upper limit of this range, the aluminum reduction continues, but, in addition, sodium begins to come off the cathode. A further increase in current density and cathode potential should increase the total production of both aluminum and sodium.

It does not appear reasonable that the mechanism of aluminum production at the cathode should change abruptly as the cathode potential becomes sufficiently high to start liberating sodium. Therefore, the theory which holds that aluminum is produced by direct cathodic reduction of an aluminum donor and that any sodium evolved from the cathode is the result of a parallel or parasitic reduction appears to be correct (10, 2). The assumption of primary sodium deposition at the cathode is no more justified in the present case than in the case of electrolysis of aqueous sodium salt solutions.

In industrial cells, sodium has been often observed. This would mean that such cells are operated at a cathodic overvoltage in excess of E_L . The only available data are those of Piontelli and Montanelli (11); they indicate that, at normal cathode current densities, aluminum cells operate at cathodic overvoltages of 0.4–0.5 v.² This is well above the values of E_L shown in Table II. Therefore, there is good reason to believe that some sodium is actually liberated at cathodes of aluminum cells.

Along the same lines, it is interesting to examine Fischer's data on running an industrial cell with an auxiliary lead cathode (23). This cell was operated at 930°–958°C, and the sodium content of the lead layer built up to 11–12%. This corresponds to a sodium activity of 0.55 (19), which is equal to the value of a_L at 945°–950°C. Sodium activity at the cathode cannot exceed a_L and any sodium produced beyond this point is free to escape. Since Fischer's pot was run under conditions representative of industrial operation, his data indicate that his pot as well as normal industrial pots liberate some sodium at the cathode.

It is reasonable to assume that evolution of sodium on a liquid aluminum cathode is governed by an overvoltage. Since sodium is a gas at cell temperatures, it is likely that its overvoltage is different from that of aluminum deposition on the same cathode. No data on sodium overvoltages in an aluminum cell are available, and therefore there is no way of predicting the amount of sodium that is produced

² In a private communication, Piontelli indicates that the above overvoltage values represent a maximum and are probably on the high side. On the basis of more recent results with improved techniques (still to be published), he estimates that, at 1000°C and 1 amp/cm², the cathodic overvoltage is of the order of 0.20 v.

as a function of current density. The effect of temperature, however, can be seen from Table II; other conditions being constant, an increase in temperature reduces the value of E_L and consequently increases the relative amount of sodium evolved. This deduction is substantiated by observations which have been made many times in aluminum reduction plants.

It is important to emphasize that the cathodic production of sodium may not be the only cause of current inefficiency in industrial aluminum cells; it may not even be the most important factor. As previously indicated, the formation of carbides, and especially monovalent aluminum compounds, may contribute substantially to loss of current efficiency. At the present time, insufficient data are available to evaluate the relative importance of each side reaction.

SUMMARY AND CONCLUSIONS

A study of sodium-aluminum equilibria in cryolite-alumina melts indicates the following:

1. Aluminum is more noble than sodium in pure cryolite or cryolite-alumina melts in the temperature range of 940°–1010°C.

2. In cryolite-base melts, the reversible deposition potential of aluminum and that of sodium at 1 atm partial pressure are close to each other. In cryolite saturated with alumina, the difference between these potentials is of the order of 0.1–0.2 v; it decreases with increasing temperature.

3. From the experimental data, it appears that, in the aluminum cell, aluminum is formed at the cathode by direct electrochemical reduction from an aluminum donor. Any sodium liberated at the cathode is the result of a parallel reduction.

4. There are indications that, in an industrial cell, the cathode overvoltage is sufficiently high to liberate some sodium.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1956 JOURNAL.

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Mechanisms of Hydrogen Producing Reactions on Palladium

III. Hydrogen Overvoltage on the Polarization and Diffusion Sides of a Cathode-Diaphragm

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ABSTRACT

Overvoltage-log current density relationships on both the polarization and diffusion sides of palladium cathode-diaphragms were measured. Effect of diaphragm thickness, cold working, and poisons were determined. It was shown that on the diffusion side, η_d is a function of the atomic hydrogen concentration, and the rate of the hydrogen producing mechanism is diffusion controlled.

INTRODUCTION

As before (1), the palladium cathode was in the form of a diaphragm separating two isolated bodies of solution. In this investigation, the current density-overvoltage relationships of the polarization and diffusion sides were determined.

Earlier (2) it was shown that the hydrogen overvoltage mechanism on the polarization side was controlled either by the combination, electrochemical, or slow discharge step depending on the pH and current density.

In addition to reporting further work on the overvoltage on the polarization side, it is the purpose of this paper to investigate the overvoltage on the diffusion side and determine its mechanism.

EXPERIMENTAL METHOD

The experimental technique used was essentially the same as that already reported (2). The electrolytic cell was the same as used in Part II (1). A rapid flow of purified hydrogen was passed through each compartment both of which contained the same solution (either 2N H₂SO₄ or approximately 0.5N H₂SO₄ + 0.5N Na₂SO₄). In the polarization compartment, current was passed between the platinum anode and the palladium cathode. The overvoltage on both the polarization and diffusion sides of the palladium diaphragm was measured against the Pt/H₂ electrodes in each compartment.

As the palladium was electrolyzed, bubbles of hydrogen, which formed on the surface, coalesced and were held by the rim of the teflon opening until a critical bubble size was reached, at which time the entire bubble left the surface. At this point the overvoltage on the polarization side was measured and the solution IR component determined by use of a current interrupter. Under steady-state current conditions these measurements gave consistent results over a reasonable period of time. Since there was no current flow in the diffusion compartment there was no solution IR drop and direct overvoltage measurements could be taken. Under constant current conditions the overvoltage measurements on both sides of the diaphragm were independent of time.

Temperature was maintained at $37 \pm 1^\circ\text{C}$. The pH of each of the sulfuric acid-sodium sulfate solutions was determined at the end of the run. The exposed area of the

palladium electrode was about 0.14 cm². Palladium diaphragms 0.0005 in., 0.002 in., 0.003 in., and 0.004 in. were used. All the diaphragms were made of annealed, hole-free palladium, except that the 0.003 in. specimen was made by cold rolling a 0.004 in. piece of foil.

RESULTS

The overvoltage-log current density relationships for both the polarization and diffusion sides of palladium diaphragms are given in Fig. 1 and 2. For the same current density, the overvoltage measured on the polarization side

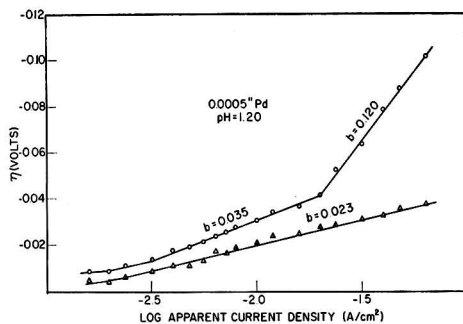


Fig. 1a. Hydrogen overvoltage on polarization and diffusion surfaces of palladium diaphragms in 0.5N H₂SO₄ + 0.5N Na₂SO₄. $\circ = \eta_p$; $\triangle = \eta_d$.

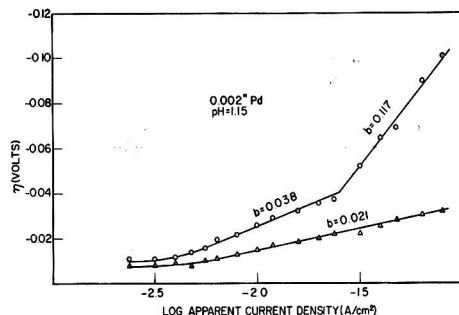


Fig. 1b. Hydrogen overvoltage on polarization and diffusion surfaces of palladium diaphragms in 0.5N H₂SO₄ + 0.5N Na₂SO₄. $\circ = \eta_p$; $\triangle = \eta_d$.

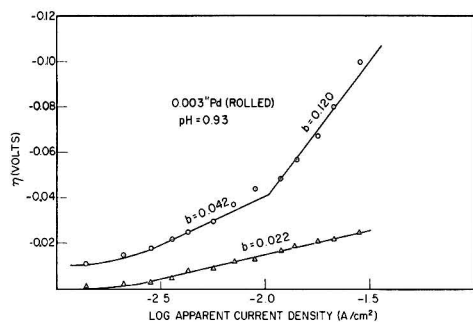


FIG. 1c. Hydrogen overvoltage on polarization and diffusion surfaces of palladium diaphragms in 0.5N $H_2SO_4 + 0.5N Na_2SO_4$. $\circ = \eta_p$; $\triangle = \eta_d$.

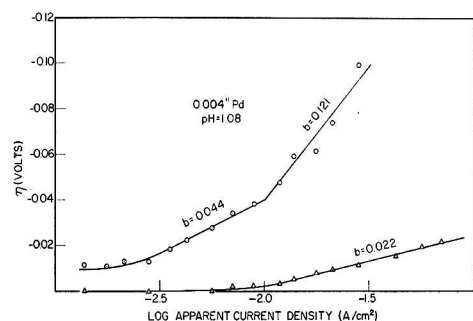


FIG. 1d. Hydrogen overvoltage on polarization and diffusion surfaces of palladium diaphragms in 0.5N $H_2SO_4 + 0.5N Na_2SO_4$. $\circ = \eta_p$; $\triangle = \eta_d$.

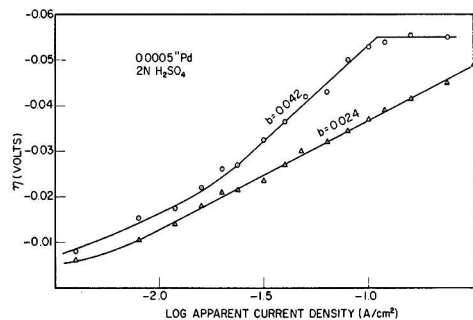


FIG. 2a. Hydrogen overvoltage on polarization and diffusion surfaces of palladium diaphragms in 2N H_2SO_4 . $\circ = \eta_p$; $\triangle = \eta_d$.

(η_p) of a palladium diaphragm was essentially the same as the η_p determined in Part II where the diffusion compartment contained ceric sulfate solution. These results confirm in general the data found for a palladium bead which was reported in Part I.

There was also a linear relationship between the overvoltage on the diffusion side (η_d) and the log of the current density with a Tafel b slope of 0.021–0.024. This slope was independent of solution and thickness of the diaphragm. Frumkin and Aladjalova (3) obtained similar results.

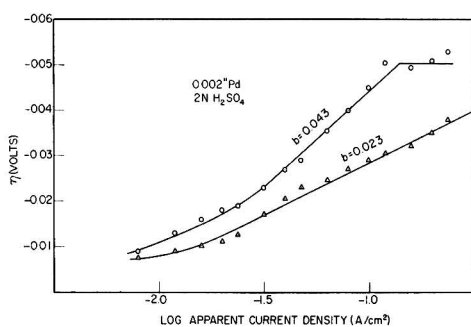


FIG. 2b. Hydrogen overvoltage on polarization and diffusion surfaces of palladium diaphragms in 2N H_2SO_4 . $\circ = \eta_p$; $\triangle = \eta_d$.

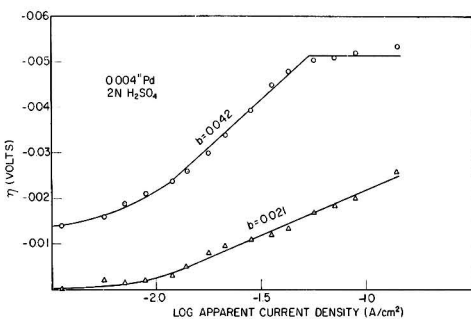


FIG. 2c. Hydrogen overvoltage on polarization and diffusion surfaces of palladium diaphragms in 2N H_2SO_4 . $\circ = \eta_p$; $\triangle = \eta_d$.

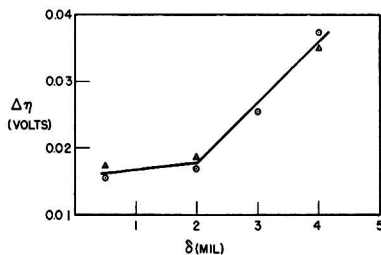


FIG. 3. Effect of diaphragm thickness on $\eta_p - \eta_d$.

The separation between the polarization and diffusion overvoltage

$$\Delta\eta = \eta_p - \eta_d$$

at the point where the mechanism of hydrogen production on the polarization side changes (the b slope changes from 0.04 to 0.12 or ~ 0) has been plotted against diaphragm thickness and is shown in Fig. 3.

On opening the circuit, the decay in η_p with time was followed for cases where the diffusion compartment either did or did not contain a strong oxidizing agent. When the solution in the diffusion compartment was 2N H_2SO_4 saturated with hydrogen, η_p reached a value of +0.046 v at the end of 19 hr. Even after this time, however, the po-

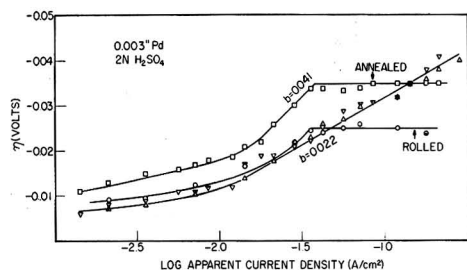


FIG. 5. Effect of cold working on hydrogen overvoltage. $\square = \eta_p$, annealed; $\circ = \eta_r$, rolled; $\nabla = \eta_a$, annealed; $\triangle = \eta_d$, rolled.

These observations present strong evidence that on the back side of the palladium diaphragm the hydrogen producing mechanism is diffusion controlled. In principle, further evidence to support this contention could be found by decreasing the thickness of the palladium diaphragm to a point where the rate of diffusion through the metal would approach a value where the rate of the combination reaction on the diffusion surface is controlling. As this critical thickness is approached the b slope should increase to 0.031 which would be the value expected if the combination reaction were rate-determining. Some evidence for just such an effect can be obtained from the b values for the 0.0005 in. compared to the thicker diaphragms. Fig. 1a and 2a show that in both cases the b value for the 0.0005 in. palladium is 0.024. Fig. 1 and 2 show also that in all cases, except one, the b value for the 0.002–0.004 in. diaphragms is either 0.021 or 0.022. If one extrapolates this apparent trend, then, at a diaphragm thickness of about 0.00005 in., the rate of diffusion should be fast enough so that the combination reaction is controlling and the b slope should be 0.031. Unfortunately, additional experimental evidence for this would be difficult to obtain since a 0.0005 in. diaphragm is about the minimum practicable thickness.

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APPENDIX I

EFFECT OF COLD WORKING ON HYDROGEN OVERVOLTAGE

A 0.004 in. thick specimen of palladium foil was cold rolled to 0.003 in. Fig. 5 shows that, in 2N H₂SO₄ solution, cold working substantially lowers the potential at which the overvoltage becomes independent of current density on the polarization side of the electrode. The electrode was then vacuum annealed at 1200°C for 3 hr. This annealing raised the levelling off point by 10 mv. The diffusion overvoltage for both the rolled and annealed specimens was the same.

Fig. 1c shows the overvoltage-log current density relationships for both front and back sides of the cold rolled palladium electrode in sulfuric acid-sodium sulfate solution. Here there is no apparent deviation from the annealed specimens shown in Fig. 1 and Fig. 3. Evidently the only major effect of cold working is to lower the potential at which the overvoltage becomes independent of current density (point at which the palladium is completely saturated with hydrogen).

More experimental work on the effect of cold working on the electrolytic properties of palladium is obviously needed before a general understanding of this system can be reached. Several investigators (4) have reported on this problem.

APPENDIX II

EFFECT OF POISONING THE POLARIZATION SURFACE ON η_p AND η_d

The polarization surface of both a platinum (0.005 in. annealed) and a palladium (0.003 in. annealed) diaphragm was poisoned with arsenic and η_p and η_d were measured. Results are shown in Table II. The clean platinum surface showed no evidence of hydrogen diffusion through the diaphragm even after polarization times as long as 5 hr. When the polarization side was poisoned, however, there was evi-

TABLE II. Effect of poisoned polarization surface on polarization and diffusion overvoltages

Current density (amp/cm ²)	Platinum (0.005 in.) in 1N H ₂ SO ₄				Palladium (0.003 in.) in 2N H ₂ SO ₄			
	$-\eta_p$ (v)		$-\eta_d$ (v)		$-\eta_p$ (v)		$-\eta_d$ (v)	
	Clean surfaces	Poisoned* polarization surface	Clean surfaces	Poisoned* polarization surface	Clean surfaces	Poisoned† polarization surface	Clean surfaces	Poisoned† polarization surface
0.00175	0.027	0.6	0	0	—	—	—	—
0.0035	0.038	0.65	0	0.001	0.015	0.15	0.0095	0.018
0.0053	0.048	0.7	0	0.002	0.016	0.17	0.010	0.019
0.025	—	—	—	—	0.028	0.25	0.020	0.023
0.050	—	—	—	—	0.035	0.27	0.027	0.028
0.100	—	—	—	—	0.035	0.29	0.033	0.030

* Added 1 ml of 0.01M As₂O₃ (area of electrode = 0.57 cm²).

† Added 0.1 ml of 0.01M As₂O₃ (area of electrode = 0.1413 cm²).

dence of a small amount of hydrogen diffusion to the back side.

Since the rate of diffusion of hydrogen through platinum is evidently very low, for a clean surface, none of the hydrogen will diffuse through the metal. However, if the rate of the combination reaction on the polarization side of the platinum is greatly lowered, as it is by poisoning, then some of the hydrogen may diffuse through the metal because the relative rates of the diffusion and combination reaction (on the polarization side) will more nearly approach one another.

The effect of poisoning the polarization side of the palladium was to raise effectively the overvoltage on the diffusion side at low current densities. However, as the current

density was increased, there was little difference between the diffusion overvoltages for clean and poisoned polarization surfaces.

Arsenic effectively destroys the catalytic activity of the molecular hydrogen-producing reactions on the palladium polarization surface. This in turn increases the atomic hydrogen concentration in the metal near the front side, hence, the diffusion gradient through the metal is greater, and the rate of flow of hydrogen through the metal is increased. For the palladium diaphragm at the higher current densities, the polarization side of the metal is completely saturated with hydrogen even on the clean surface; therefore, there is no effective increase in the diffusion gradient on poisoning.

Measurement of the Acidity of Aqueous Solutions at High Temperatures and Pressures

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ABSTRACT

The potential of a platinized platinum-hydrogen electrode in two dilute hydrochloric acid solutions was measured with respect to a silver-silver chloride electrode from room temperature to 250°C at a total pressure from atmospheric to 600 psig.

A fused quartz cell was employed inside a steel bomb which contained the vapor pressure of the electrolyte plus the added hydrogen pressure.

The silver-silver chloride electrode was a silver plated and chloridized platinum gauze at the bottom of the cell. The hydrogen electrode was half immersed in the solution at the top.

The results were reasonably reproducible and permit estimating the acidity of the solution within approximately 0.1 to 0.2 pH units. The results agree reasonably well with theoretical calculations from the Debye-Hückel theory by Lietzke.

INTRODUCTION

Most of the electrode systems used for pH measurement are satisfactory only near room temperature, and none of them seems to have been applied or tested above 100°C.

However, control of aqueous reactions, such as hydrolyses and esterifications in chemical industry, and maintenance of aqueous solutions, such as boiler waters and nuclear reactor solutions, make continuous and rapid pH measurement at high temperatures and pressures desirable. The range of interest reaches to the critical point, but room temperature to about 250°C and up to a pressure of 600 psia covers most cases. An electrode system suitable for rapid and continuous measurement of pH over wide ranges of temperatures and pressures would evidently be of considerable interest.

The effect of high pressure on electrode potential has received little attention. No appreciable effect on electrodes involving only solids and liquids would be expected at the usual commercial process pressures. When a gas is involved in the electrode reaction, a definite effect on the fugacity, and thus on the electrode potential, is predicted by the Nernst equation. The most pertinent experimental work

is that of Hainsworth, Rowley, and MacInnes (1), who found that up to 9000 psia a cell at 25°C containing a hydrogen electrode and a HgCl electrode obeys the usual Nernst equation very closely. Above that pressure increasing deviations occur.

The effect of high temperature has also been investigated very little, although three studies are pertinent. The antimony electrode is the only one that has been used for pH measurements well above room temperature. It is used for measuring the pH of cane juices from 80° to 100°C and covers the range of pH 2 to 12 (2).

Myers (3) studied the antimony electrode against a silver-silver chloride electrode and found an irreversible effect from 30° to 50°C, but obtained fairly reproducible emf measurements from 60° to 100° C. He applied nitrogen to obtain a total pressure of 2000 psi and carried the electrode system up to 300°C. These results were reproducible, but yielded the irregularities shown in Fig. 1. The breaks in the curve may be due to the formation of different hydrates with differing solubilities as the temperature is raised. This would seem to be an undesirable effect, and antimony electrodes cannot be expected to be serviceable above 100°C.

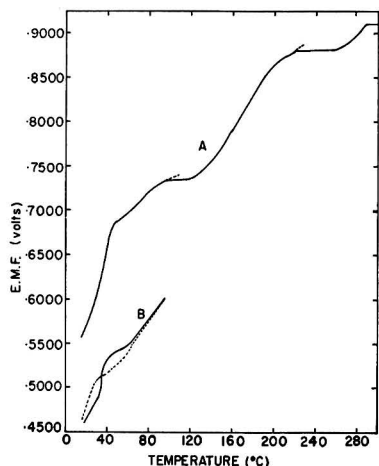


FIG. 1. EMF-temperature relationship (3) for the antimony-silver chloride cell in a buffered solution, pressurized with nitrogen. Curve A, pH = 7.0 at 25°C; total pressure = 2000 psia; curve B, pH = 4.0 at 25°C; total pressure = 14.7 psia.

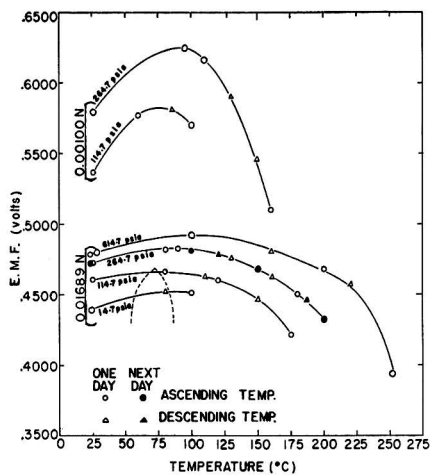


FIG. 2. EMF of the hydrogen-silver chloride cell in dilute aqueous hydrochloric acid as a function of temperature, pressure, and concentration. Dashed line is observed emf for the silver chloride thermogalvanic cell vs. temperature in °C, with 0.1N HCl and one electrode at 25°C (4).

Levin and Bonilla (4) set up a thermogalvanic cell with one AgCl electrode at room temperature (25°C) and another at temperatures up to 90°C, measuring the temperature coefficient in several different electrolytes. In hydrochloric acid solution these were found to increase at first with increase of temperature, pass through a maximum at about 72°C, and then decrease (Fig. 2).

Bonnemey (5) studied the H₂ electrode at a total pressure of 14.7 atm abs and found the electrode voltage to be linear with temperature over a range of 35°C.

The present study was aimed at determining the suitability of a hydrogen electrode and a silver-silver chloride

electrode for acidity determinations in a single compartment cell at temperatures up to 250°C and total pressures up to 600 psig.

APPARATUS

The apparatus is shown in Fig. 3. The cell was of fused quartz. A platinum lead-in wire sealed through the bottom connected to a gauze in the lower compartment. The cell was open at the top, so inner and outer pressures were equal.

A steel bomb with $\frac{3}{8}$ in. walls to withstand the high temperature and pressure served as container for the cell. A 27 in. length of nominal $\frac{1}{2}$ in. iron pipe was screwed into the top of the bomb and a fitting with four tapped connections was mounted on its top. A spark plug at the top served as lead-in and support for the hydrogen electrode. A hole on one side of the top fitting connected to a hydrogen cylinder, and one on the other side to a vacuum pump and a manometer. The long stem on the cell and bomb was cooled at the middle so as to prevent evaporation from the electrolyte and condensation on the insulation at the top.

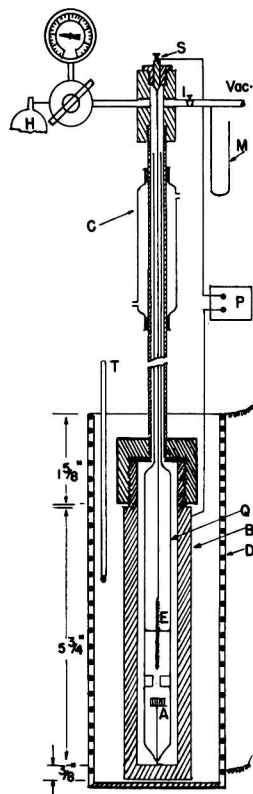


FIG. 3. Cell and bomb used in high pressure tests with the hydrogen-silver chloride electrode system. A—AgCl electrode; B—steel bomb; C—condenser; D—heating jacket; E—platinized platinum electrode; H—hydrogen cylinder; I—gas outlet valve; M—manometer; P—potentiometer; Q—quartz cell; S—spark plug; T—thermometer.

The bomb and quartz cell were brought to and maintained at the desired temperature by an external electrical resistance wire heater.

The platinum gauze, $\frac{1}{2}$ in. on a side, was plated and chloridized to provide an Ag, AgCl electrode. The short platinum lead from the Ag/AgCl electrode was connected to a pure thermocouple-iron wire attached to the inside wall of the bomb. The hydrogen electrode was a spiral of platinumized platinum half-immersed in the electrolyte. It hung by another iron wire from the central terminal of the spark plug. Other iron wires led from the outside of the bomb and from the spark plug terminal to a potentiometer. All connections were silver-soldered.

The platinum-iron junctions at the hydrogen electrode and the silver electrode nullify each other's thermoelectric effect, and no difference from platinum or silver leads is obtained.

EXPERIMENTAL PROCEDURE

Solutions of hydrochloric acid were prepared by diluting reagent-quality acid. The pH of each solution was measured with a Beckman pH meter at room temperature. Normality of each solution was determined by titrating with standard alkali.

The platinum gauze in the cell was cleaned by washing several times with boiling nitric acid and then rinsing thoroughly with distilled water.

The compositions of the strike solution and the plating solution for the silver plating were taken from Promisel and Wood (6). The platinum gauze was silver plated for $\frac{1}{2}$ min in the strike solution and then for 15 hr in the plating bath, using a silver anode and a current of 8 ma. After removal from the plating bath, it was washed frequently with distilled water for one week to remove adsorbed contamination (7).

After the washing it was chloridized anodically in molar hydrochloric acid at 5 ma for 1 hr (8). It was then washed repeatedly with distilled water and kept in very dilute hydrochloric acid for a week to complete the aging (8). Eight silver foils of the same size were simultaneously chloridized in the same way. Five of the eight silver electrodes were found to agree with each other within 0.1 mv in dilute HCl, the other 3 not being much farther off. This agreement showed that the chloridizing conditions were correct. More accuracy (0.02 mv), as claimed by Smith and Taylor, might have been achieved with more precaution and with improvements in the methods of measurements, but for the present purpose it was considered unnecessary.

Two pieces of 0.025 in. platinum wire one inch long were wound in the form of a narrow spiral and cleaned by repeated heating in a Bunsen flame and dipping in concentrated hydrochloric acid. The platinumization was carried out by electrolysis at room temperature of a solution containing 3% chloroplatinic acid, using the two platinum spirals alternately as cathode and anode with a 2-v storage battery as an energy source.

When the two spirals were covered with a fairly thick, black velvety deposit, they were removed and washed with water. To remove adsorbed oxygen, the electrodes were reduced cathodically for 15 min in very dilute sulfuric acid, using a platinum anode and the 2-v battery. The

process was repeated with distilled water and then the electrodes were stored in distilled water.

A L&N type K-2 potentiometer and wall galvanometer were used to measure the emf.

The desired total pressure was maintained by supplying hydrogen from a cylinder through a Hoke high pressure gas regulator. A standard rubberized asbestos high temperature gasket was used at the top of the bomb. The threaded pipe joints were made tight with pipe dope. The whole assembly was sufficiently leak proof that pressure could be maintained sensibly constant for 48 hr with valve I and the hydrogen cylinder shut off.

The pressure was always kept well above the vapor pressure of water to prevent boiling of the solution. Decreases in temperature or pressure were always made very slowly to prevent any possible foaming of the electrolyte up the tube. An hour was allowed at each new temperature and pressure change to ensure equalization of the temperature and concentrations throughout the cell.

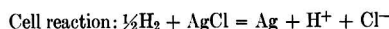
RESULTS AND DISCUSSION

The potential of the cell was measured at several high temperatures and pressures with solutions of hydrochloric acid that were 0.00100 and 0.01689*N* at room temperature. The emf values with ascending and descending temperatures are seen to agree closely in Fig. 2, demonstrating the good reversibility of the electrode system.

The electrode system also yielded excellent reproducibility over longer intervals as shown by the solid points in Fig. 2, which were obtained one day later.

Accuracy of the experimental set-up was shown by the fact that cell potentials at atmospheric pressure and room temperature for the two concentrations here studied fall on the same smooth curve of emf vs. concentration given by Harned and Ehler's measurements (9) at the same conditions.

The Nernst equation should apply to all ionic cells under any conditions. For this cell:



$$\text{Cell potential: } E = E^\circ - \frac{RT}{F} \ln \frac{(m\gamma_{\pm})^2}{\sqrt{P'}} \quad (1)$$

where m = molality of the HCl solution, γ_{\pm} = average activity coefficient of H^+ and Cl^- ions, and P' = fugacity of the hydrogen.

Lietzke (10) calculated and plotted the potentials given by equation (1) for 0.01689*N* HCl and these same experimental conditions. E° was obtained by extrapolating Harned and Ehler's values vs. temperature. The activity coefficient of HCl at high temperatures was calculated by two methods.

(a) The thermodynamic relation

$$\left(\frac{\delta \ln \gamma_{\pm}}{\delta T} \right) = \frac{\bar{L}_2}{\nu RT^2}$$

was integrated with the required temperature correction over the interval from 0° to 250°C to yield γ_{\pm} in 25°C steps. \bar{L}_2 is the relative partial molal heat content of the HCl in the solution.

(b) The Debye-Hückel equation was used (9) in the form

$$-\log \gamma_{\pm} = \frac{1.8123 \times 10^6 \sqrt{C}}{(DT)^{3/2}} \cdot \frac{1}{1 + 50.288 \times 10^8 (DT)^{-1/2} a_i \sqrt{C}} \quad (\text{II})$$

D is the dielectric constant, C is the hydrogen ion concentration in moles per liter, and the distance a_i of closest approach of the ions was taken as 5×10^{-8} cm.

The activity coefficients calculated by the two methods differed by a maximum of 0.6%, corresponding to a maximum variation in the calculated potentials of 0.4 mv.

The hydrogen partial pressures were converted to fugacities by using the data of Deming and Shupe (11) and by assuming that the water vapor does not affect the fugacity of the hydrogen. At the highest hydrogen partial pressures the correction amounted to about 3%.

Lietzke's values are plotted in Fig. 4 for comparison with the experimental data. Calculated and experimental potentials are seen, in general, to agree within a few millivolts.

Hydrogen was found to have considerable effect on the potential of AgCl electrodes. To measure its effect two AgCl electrodes were set up in the same 100 ml beaker and another in a different beaker. The beakers were connected by a bridge containing the same solution but not permitting appreciable hydrogen diffusion between the vessels. The potential between any two of the Ag/AgCl electrodes was under 0.1 mv. Hydrogen was then bubbled, at atmospheric pressure and temperature, past one of the two electrodes in the same beaker. This electrode became 2.3 mv more negative than the other electrode in the same beaker, and 7.6 mv more negative than the third electrode, in the other beaker. This diminution by hydrogen of the potential of an AgCl electrode toward that of a hydrogen electrode may be due to the coexistence of simultaneous hydrogen and AgCl electrodes at the hydrogenated AgCl electrode, yielding an intermediate potential which depends on the resistance and overvoltage characteristics of each electrode reaction. The effect seemed to be reversible, since a good potentiometer balance was readily obtained. It is presumably reproducible, since interchanging any two

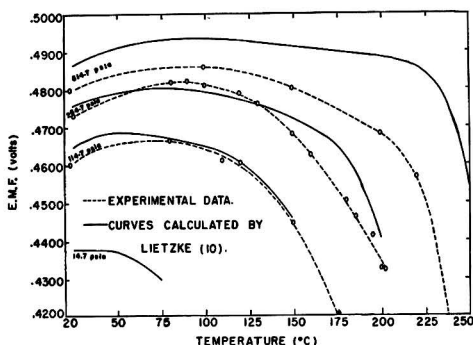


FIG. 4. Theoretical (10) and experimental values of emf of the hydrogen-silver chloride cell in 0.01689N HCl.

AgCl electrodes yielded the same result. This effect would be more pronounced at the higher temperatures, due to higher solubility and higher diffusion rate of hydrogen gas, and also at a higher hydrogen pressure at a given temperature.

Lietzke points out that hydrogen reduction of part of the AgCl in an AgCl electrode would increase the acid concentration in the AgCl coating and, hence, would lower the potential of the system. This is another possible explanation.

EFFECT OF HYDROGEN PRESSURE ON OVER-ALL CELL POTENTIAL

The curves of Fig. 2 have been crossplotted in Fig. 5 to show the effect of hydrogen pressure on the over-all cell potential at constant temperature. The lower limit of the curves at the boiling point of the electrolyte is shown dotted, for orientation purposes.

Neglecting the effect of H_2 on the AgCl electrode and considering the over-all reaction as involving gaseous hydrogen in an ideal state, the difference in emf values of the over-all cell at constant temperature and two different hydrogen partial pressures may be represented as follows:

$$E_{P_2} - E_{P_1} = \frac{RT}{2F} \ln \frac{P_2}{P_1} \quad (\text{III})$$

Fig. 6 has been plotted for P_2 constant at 614.7 psia. With the coordinates employed, equation (III) is a straight line through the origin with a slope of unity. While the present 25°C curve agrees somewhat with equation (III), it is evident that, at the higher temperatures, agreement is quite poor. From Hainsworth's work it is evident that the deviation from equation (III) does not occur at the hydrogen electrode. Abnormalities in solubility or crystalline form of the AgCl would not show up as deviations unless they were functions of hydrogen pressure, which seems unlikely. The only remaining possibility seems to be a reproducible, nonequilibrium condition in which hydrogen electrode sites are established in the Ag electrode itself, as previously suggested. At constant pressure this

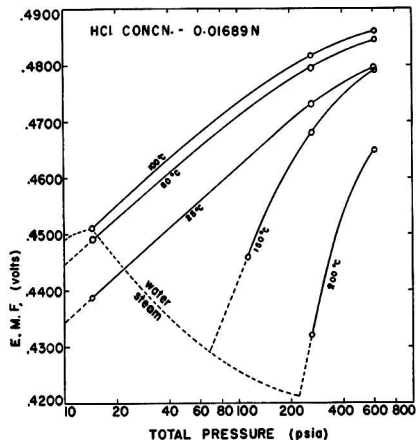


FIG. 5. EMF of the hydrogen-silver chloride cell in 0.01689N HCl vs. pressure and temperature.

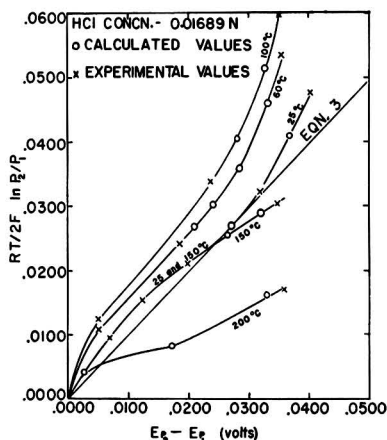


FIG. 6. Effect of hydrogen on the hydrogen-silver chloride cell voltage, in terms of pressure. $P_2 = 614.7$ psia.

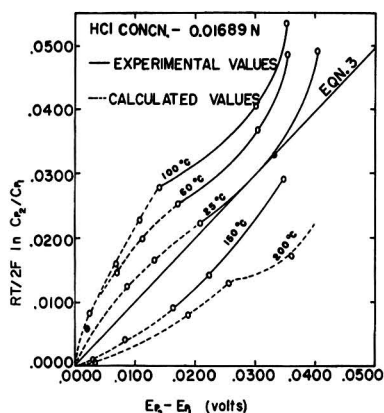


FIG. 7. Effect of hydrogen on the hydrogen-silver chloride cell voltage, in terms of concentration. $P_2 = 614.7$ psia.

would be expected to decrease the cell potential more the higher the temperature (witness the trend to the left from 25° to 100°C). At constant temperature it should decrease the potential more the higher the pressure (see the upward curvature at the end of the 25° to 100°C isotherms). No explanation is evident for the voltage increase at 150° and 200°C.

Mercury is noted for high hydrogen overvoltage, which may be the reason for the apparent lack of effect of hydrogen on Hainsworth's calomel electrode. In addition, the calomel bed was evidently deep, while these electrodes had only the usual thin AgCl coating and were probably less effective in preventing diffusion of dissolved hydrogen to the silver.

Assuming that γ_{H_2} , a_{H^+} , and a_{Ag^+} remain constant at a given temperature over the range of hydrogen partial pressures from P_1 to P_2 , correction for variation in hydrogen pressure may be made by writing

$$E_{P_2} - E_{P_1} = \frac{RT}{2F} \ln \frac{C_{P_2}}{C_{P_1}} \quad (IV)$$

where C_P = solubility of hydrogen at the specified pressure. Fig. 7 is a check of equation (IV). No improvement in correlation is evident. This plot is of additional interest in view of Rideal and Bowden's finding (12) that overvoltage (ΔE_0) is a linear function of the logarithm of the polarizing current, equivalent to the rate of hydrogen diffusion through the AgCl coating. Thus

$$\Delta E_0 = a + b \log I = c + d \log (C_{H_2}) \quad (V)$$

and one might expect isotherms on Fig. 7 to be straight, assuming constancy of the AgCl coating, even when they did not agree with equation (IV). It is seen that equation (V) does not bring these data into agreement.

PRACTICAL CORRELATION OF CELL VOLTAGE AGAINST ACIDITY

In the cell Pt(H₂)/HCl, AgCl/Ag there are four variables, viz., concentration of HCl, temperature, pressure, and emf, of which one (generally considered the emf) is dependent on the other three. In a graphical correlation, or calibration curve, two independent variables and one dependent variable, at the most, can be conveniently represented. It has already been shown that a correlation eliminating the effect of pressure could not be obtained, and none would be expected that corrects for temperature, on account of the complicated effect of temperature on the over-all cell. Therefore, it is desirable to attempt to include the effect of acid concentration on the cell voltage as a theoretical correction to the observed voltage.

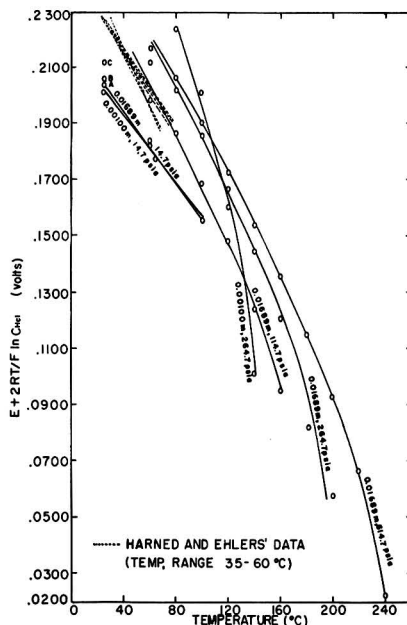


FIG. 8. Effect of HCl concentration on cell voltage—calibration curves for hydrogen-silver chloride cell for pH determination in dilute aqueous HCl solution. Dashed lines show data calculated from Harned and Ehler.

In this cell the effect ΔE_c on the cell potential due to a change from ionic activities of unity may be represented by

$$\begin{aligned}\Delta E_c &= -\frac{RT}{F} \ln (C_{H^+} \gamma_{H^+} \cdot C_{Cl^-} \gamma_{Cl^-}) \\ &= -\frac{2RT}{F} \ln (C_{HCl} \gamma_{\pm})\end{aligned}$$

Taking the right-hand side as the concentration correction and subtracting it from the cell emf, the effect of concentration should vanish. If this correction is valid, plotting $(E + 2RT/F \ln C_{HCl} \gamma_{\pm})$ vs. temperature should yield the same curve for different concentrations at the same pressure.

Compared to an activity coefficient of unity, predicted values of γ_{\pm} would only change ΔE_c by a maximum of 6 to 7 mv in the case of the 0.01689*N* HCl solution and less in the more dilute solution. As this difference in ΔE_c is less than the apparent experimental uncertainty, γ_{\pm} was assumed unity for simplicity (Fig. 8).

The dashed lines on the top of Fig. 8 are calculated from the data of Harned and Ehler at 35°–60°C (9). The rest of the curves represent the present data. The concentrations of HCl in Harned and Ehler's work lie between the two concentrations used in the present experiments. The present two lines at atmospheric pressure agree with each other, as do the lines of Harned and Ehler, but the average discrepancy between the two sets of lines is about 20 mv. This discrepancy must be due to the effect of hydrogen on the AgCl electrode, as described before. To show in Fig. 8 the magnitude of this effect as here observed, points *A*, *B*, and *C* have been plotted. The distance *AB* is the potential difference between the electrode in the stream of H₂ bubbles and the other one in the same beaker, and *AC* is the potential difference between the electrode in the H₂ stream and the one in the separate container. Although these potential differences are well under the 20 mv discrepancy, it is quite possible that the AgCl electrode in the quartz cell had a thinner AgCl deposit and a larger hydrogen correction than the ones prepared and tested externally.

The lines at 264.7 psia cross, but do not coincide as might have been desired. However, except for the 264.7 psia line for the dilute solution, the lines constitute a reasonably smooth family. Accordingly, a plot of the form

of Fig. 8 seems to constitute a satisfactory calibration curve for a given hydrogen/AgCl cell.

In conclusion, the one-compartment hydrogen/AgCl cell is not ideal for pH measurement at high temperatures and pressures, due apparently to a slight polarization of the AgCl electrode by the hydrogen. However, when directly calibrated or reproducibly manufactured it is apparently suitable, at least up to 250°C, for pH determination to within better than 0.2 pH units. Its sensitivity is yet greater, so that still smaller variations in acidity in a process stream could be detected. Fig. 8 should be fairly reliable for electrodes made as herein described. Probably a two-compartment cell which prevents hydrogen from reaching the AgCl electrode would be slightly more accurate.

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Oxygen Overvoltage in Concentrated Acid Solutions

I. Perchloric Acid

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ABSTRACT

Oxygen overvoltage was measured on platinum electrodes in 5M perchloric acid from -45° to $+40^{\circ}\text{C}$ and in 0.005–9M perchloric acid at 0°C . A limiting current density that was found is due to activation overvoltage at the anode surface. This limiting current density decreased at lower temperatures and in higher perchloric acid concentrations. It also marked the beginning of ozone formation. Adsorption of perchlorate ions is believed to be the cause of the limiting current density.

INTRODUCTION

Although most commercial electrolysis reactions are carried out in concentrated electrolytes, little work on anodic overvoltage has been done in concentrated electrolytes. To fill this gap partly, anodic overvoltage was studied in concentrated perchloric acid solutions in connection with prior work (1) on electrolytic ozone. Platinum and platinum-iridium alloy were chosen for anodes because they give the highest yields of ozone.

In general, overvoltage at an electrode may be resolved into three components (2): (a) an ohmic IR drop, η_o , through a film on the electrode surface or through the electrolyte adjacent to the surface; (b) concentration polarization, η_c , caused by difference in concentration of electrolyte between the bulk solution and the electrode surface; and (c) an activation overvoltage, η_a , associated with the rate-controlling step at the electrode surface. The total overvoltage, η , is the sum of these three terms:

$$\eta = \eta_o + \eta_c + \eta_a$$

The relation of activation overvoltage to ozone formation will be shown.

Considerable controversy is evident in the literature regarding the mechanism of electrolytic oxidations (3). There are two general mechanisms postulated to explain electrolytic oxidation reactions in aqueous media: (a) formation from discharge of OH^- ions or water molecules of an intermediate oxidizing agent common to all reactions which accomplishes the reaction chemically; and (b) direct discharge of the reacting ions. The intermediate oxidizing agent has been attributed by various investigators to be oxygen (4), atomic oxygen (5), hydrogen peroxide (6), and hydroxyl radical (7). Experiments of Butler (8, 9) and Hickling (10) indicate that a layer of adsorbed oxygen or platinum oxide is formed on platinum anodes prior to oxygen evolution. The direct discharge theory has become more plausible since the chemistry of free radicals has become better known (11).

EXPERIMENTAL APPARATUS AND PROCEDURE

Electrodes.—Pure platinum and 95% platinum-5% iridium alloy were used as anode materials in all the experimental work. Platinum anodes have been found to give the highest yield of ozone (1) which has been believed to be the result of the high oxygen overvoltage associated with them. The platinum-iridium alloy which behaves similarly is used extensively in the electrochemical industry because of its better corrosion resistance (12). Several anodes were used in the form of wire, tube, and sheets. Inert cathodes of platinum, platinum-iridium, or palladium-gold were used.

Cells.—The two cells used in most of this work are shown on Fig. 1 and 2.

Cell A was a tall 200-ml beaker fitted with a rubber stopper supporting the electrodes and Luggin capillary. An annular palladium-gold alloy cathode surrounded the anode to give a uniform anode current density. Several different anodes were used. The first was a 0.30 cm OD 95% platinum-5% iridium tube with 3.08 cm² exposed area. It was sealed to a glass tube and plugged with a glass bead at the lower end. All electrical contacts to the glass sealed platinum electrodes were made with mercury. The temperature of this hollow anode was measured by means of a thermocouple within it. The second anode was a 0.71 mm platinum wire with 0.38 cm² exposed area, also sealed to a glass tube. The third anode was a 0.14 cm platinum wire with 0.12 cm² exposed area. It was fastened in a paraffin insulated steel shaft which was rotated by an electric stirring motor.

Cell B was designed for simultaneously measuring ozone concentration and overvoltage. The electrolyte volume was 21.0 ml and there was a minimum volume for gas. The anode was a 0.30 cm OD 95% platinum-5% iridium tube with an exposed area of 6.10 cm². Teflon gaskets held under compression by brass stay bolts exterior to the cell formed a liquid-tight seal at each end of the cell. A tube was provided for filling the cell and sampling electrolyte. The cathode, a length of 0.71 mm platinum wire, entered through a Teflon sealed capillary tube and traversed the length of the cell on each side of the cell parallel to the anode to give a uniform anode current density.

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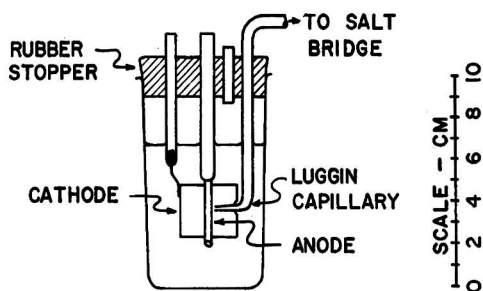


FIG. 1. Cell A, for measurement of anodic overvoltage

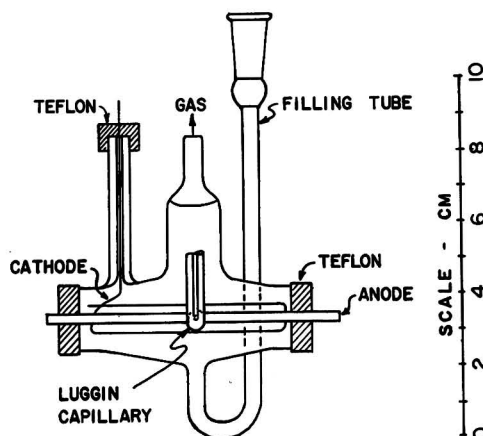


FIG. 2. Cell B, for simultaneous measurement of ozone concentration and overvoltage.

Electrical circuit.—The power supply for the cells was a 50 v lead acid storage battery. Current was measured with a Weston Model 785 industrial circuit tester which had 50 microamp, 1, 10, and 100 milliamp, and 1 and 10 amp scales. Potentials were measured with a Leeds and Northrup student type potentiometer. A vernier decade resistance box was constructed to vary the current from 0.000001 to 10 amp continuously without breaking the circuit. Anode potential was measured on each of the cells by means of a Luggin capillary connected through salt bridges to a saturated potassium chloride calomel electrode.

Salt bridge and calomel cell.—A saturated potassium chloride calomel electrode was used as reference electrode because of its reliability and simplicity. Hydrochloric acid was used as intermediate connecting solution to the perchloric acid electrolytes in order to avoid formation of insoluble potassium perchlorate at a perchloric acid-potassium chloride junction. The bridge was a 1 mm ID glass tube filled with sintered glass to minimize liquid flow through it.

The calomel cell and liquid-liquid junctions were calibrated against an hydrogen electrode in the electrolytes studied because there is no exact method of calculating junction potentials. The temperature of the calomel electrode and liquid junctions was held at 25°C, while the

temperature of the electrolyte and hydrogen electrode was varied over the full range of temperatures under which overvoltage was studied.

The reversible oxygen potential for various temperatures was calculated from an expression for the free energy of water decomposition (13). The reversible potential was not corrected for the small deviation due to the change in the activity of water in the concentrated electrolyte solutions. The deviation of the water activity from unity in 5M perchloric acid at 25°C (14) causes an error of only 0.006 v.

Ultraviolet photometer for ozone determination.—An ultraviolet photometer similar to the instrument described by Klotz (15) was constructed to measure ozone concentration. The instrument calibration was based on the Lambert-Beer law and the known extinction coefficient of ozone at a wave length of 253 m μ (16) and was checked by idometric titration. The 1-cm thick sample cell allowed rapid and accurate measurement of ozone from 0.1 to 3 wt % concentration.

EXPERIMENTAL RESULTS

This study followed an observation of a limiting current density shown on Fig. 3 for a cell used to prepare electrolytic ozone. The cell [shown in Fig. 1 in prior work (1)] had a 2.8 x 1.0 cm sheet platinum anode. The relation shown in Fig. 3 was obtained with 5M perchloric acid

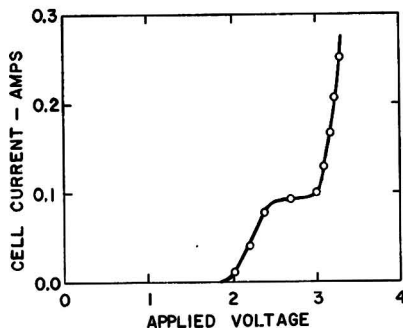


Fig. 3. Current-voltage curve for ozone cell

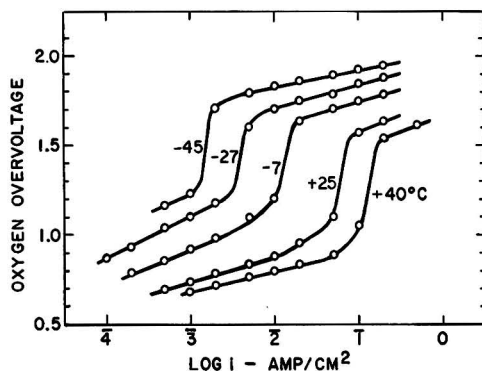


FIG. 4. Oxygen overvoltage in 5M perchloric acid. Effect of temperature.

TABLE I. Values of b in Tafel equation, 5M HClO₄ electrolyte

Temp, °C	-45	-25	-7	+25	+40
b , lower line	—	0.26	0.22	0.14	0.11
b , upper line	0.11	0.15	0.14	—	—

at 0°C. The apparent limiting current density was most unexpected because there was no ionic specie present which would be expected to give rise to concentration polarization, the usual cause of a limiting current density.

Overvoltage in 5M perchloric acid—temperature effect.—The limiting current density was found to be an effect occurring entirely at the anode. Fig. 4 shows oxygen overvoltage determined in 5M perchloric acid at several temperatures with cell A, using the 3.08 cm² platinum-iridium alloy anode. Temperature was controlled by a methanol-solid carbon dioxide bath below 0°C and a water bath at higher temperatures. The oxygen overvoltage at a given temperature was correlated by the Tafel equation, $\eta = a + b \log i$, above and below the limiting current density.

Slopes of the upper and lower Tafel lines are shown on Table I. The lower lines below 0°C have unusually large slopes. It may be noted on Fig. 4 that there is about a one hundredfold variation in the limiting current density between -45° and +40°C.

The experimental procedure followed in obtaining the curves on Fig. 4 was to pre-electrolyze for 1 hr or more at a current density of 0.1–1.0 amp/cm² to reach a steady-state potential. The potential was then recorded and the current was reduced by a small increment, taking care not to break the circuit. The potential was again recorded when it became "approximately constant." This was repeated for each of the points. "Approximately constant" was defined as it was by Hickling and Hill (17) to be a potential change of less than 0.01 v in 30 min, or 0.0003 v/min. The procedure of descending current density was used because of the much shorter time required for the potential to become approximately constant. Essentially the same steady-state values were obtained with ascending current density, but only after a longer period of time. Above and below the region of the limiting current density a steady-state condition was reached within 5 or 10 min, while in the transition region 1 hr or more was required for the potential to become approximately constant.

The limiting current density is displaced to a higher value upon either increasing or decreasing the current in rapid successive steps. The overvoltage tends to follow the lower line past the limiting current density if the current is rapidly increased. If the current is then held constant, the potential rises slowly to the upper line. When the limiting current density is approached from above on the upper line by rapidly decreasing the current, the potential will drop to the lower line at a current greater than the limiting current density. Again, if the current is held constant here, the potential will rise slowly back to the upper line.

Effect of electrolyte concentration.—The effect of perchloric acid concentration at a temperature of 0°C is shown on Fig. 5. These data were obtained with cell A and the

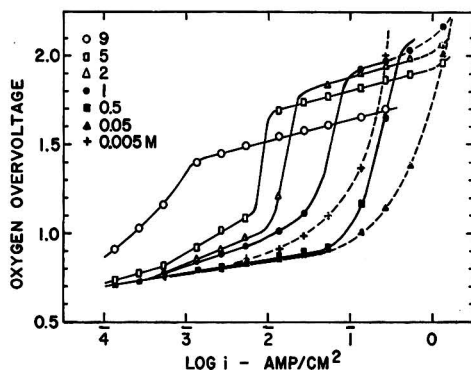


FIG. 5. Oxygen overvoltage at 0°C. Effect of perchloric acid concentration.

0.38 cm² wire anode. The following may be observed on Fig. 5:

1. The limiting current density decreases in higher perchloric acid concentration.
2. At low current density, overvoltage for all concentrations approaches the same limiting curve.
3. The slope of the upper curves is independent of concentration. The slopes of the upper and lower Tafel lines are presented in Table II.
4. The overvoltage of the upper curves decreases with increased perchloric acid concentration at a given current density.
5. At concentration less than 0.5M, ohmic overvoltage becomes appreciable before the limiting current density is reached due to increased electrolyte resistance. This was demonstrated by plotting the difference between the observed overvoltage and the extrapolated lower Tafel line against current density for the 0.05 and 0.005M solutions. A linear relation was obtained that was not found at higher concentration. It is noted on Fig. 5 that there is a deviation from the upper Tafel lines at about 1 amp/cm² for higher concentrations which can be traced to ohmic overvoltage. Therefore, the limiting current density reported here at concentrations above 0.5M is not due to ohmic overvoltage.

Overvoltage with rotating electrode.—The limiting current density was shown not to be due to concentration polarization by use of a rotating anode. Exactly the same curve was produced in 5M perchloric acid at 25°C with the 0.12 cm² electrode stationary as with a rotation of 500 rpm. Rotation of the anode would reduce the film thickness and hence increase the limiting current density. The identical values indicate that the limiting current density is not diffusion controlled.

Since the limiting current density is due neither to ohmic nor to concentration overvoltage, it must be an

TABLE II. Values of b in Tafel equation, perchloric acid at 0°C

Conc. M	0.005	0.05	0.5	1	2	5	9
b , lower line	0.07	0.07	0.075	0.15	0.20	0.27	—
b , upper line	—	—	—	—	0.12	0.12	0.12

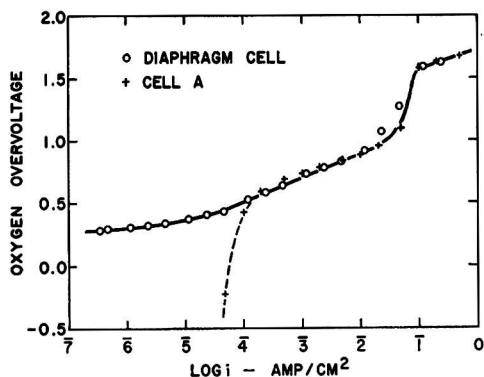


FIG. 6. Oxygen overvoltage extended to low current densities with cell A and with diaphragm cell.

activation overvoltage due to a change in the electrode surface reaction.

Overvoltage with diaphragm cell.—An experiment with a diaphragm cell showed that the limiting current density is not due to depolarization of the anode by diffusion of hydrogen from the cathode. Fig. 6 shows the oxygen overvoltage over an extended range of current density in 5M perchloric acid obtained with cell A without a diaphragm and a second cell (not shown) with diaphragm to restrict mixing of catholyte and anolyte. Below 0.0001 amp/cm² with cell A the overvoltage fell to negative values due to depolarization by hydrogen formed at the cathode. This agrees with the results of Hickling (18), who showed experimentally in 1M hydrochloric acid and analytically from diffusion theory, that the limiting current density for diffusion of oxygen dissolved at 1 atm was about 0.0001 amp/cm². The same order of magnitude of this limiting current density would be expected for both hydrogen and oxygen diffusion. Above 0.001 amp/cm² in unstirred solutions Hickling found that the dissolved oxygen had no effect on hydrogen overvoltage. Similarly in this work the curve for cell A and for the diaphragm cell coincided above 0.001 amp/cm². The limiting current density due to the electrode surface reaction occurred at the same point in both cells. The leveling of the non-depolarized curve at low current density at a potential above the reversible oxygen potential is in accord with data of Hickling and Hill (17).

Electrode reactions.—Anodic products under various conditions of temperature and current density were investigated to clarify the chemistry of the anode reactions. **Ozone formation.**—A study was made in the region of the limiting current density using cell B, designed for simultaneous measurement of ozone concentration and overvoltage. Prior work on electrolytic ozone (1) was done at low temperatures and at current densities well above the limiting current density and gave no indication of behavior in this region.

Fig. 7 shows the relationship of ozone formation to the overvoltage curve. Ozone, it is seen, is first detected at the point where the slope of the lower overvoltage line

deviates from the Tafel correlation. The current efficiency for ozone formation (equivalent to the weight per cent ozone in the anode gas) goes through a maximum of about 4% at the point of inflection of the overvoltage curve. This can be seen by comparison to the plot of the slope of the overvoltage curve. The ozone current efficiency goes through a minimum as the current density is further increased. A still further increase in current density will raise the current efficiency to better than 30% as has been reported previously (1).

The same relation of ozone production to the limiting current density was found to hold for other perchloric acid concentrations. The height of the current efficiency maximum appeared to increase in higher concentration electrolytes and lower temperatures. These curves were reproducible with ascending or descending current density if the current was changed slowly without interruption and a sufficient time was allowed to reach steady state. Rapidly increasing the current density caused the initial point of ozone detection to be displaced, corresponding to the increase in the limiting current density. The maximum of the transient ozone concentration curve was also higher than the steady-state curve.

Chlorine dioxide formation.—Chlorine dioxide was detected by its yellow color in the electrolyte and anode gas in the electrolysis of 9M perchloric acid above the limiting current density. This is in agreement with the work of Grube and Mayer (19) who showed that electrolysis of 11.4M perchloric acid at 0.22–0.75 amp/cm² with platinum electrodes at 0°C produced chlorine dioxide and chloric acid at current efficiencies up to 10%. More oxygen was obtained than could be accounted for by the electrolysis of water. They explained this by the following reactions

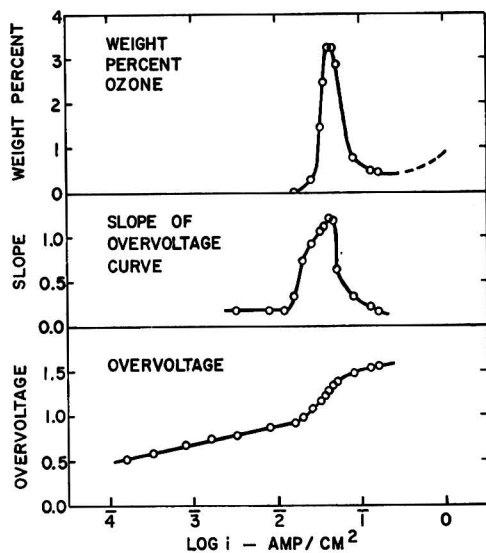
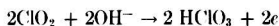
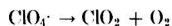
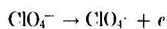


FIG. 7. Relationship of initial ozone concentration to the overvoltage curve.

involving direct discharge of perchlorate ion to form perchlorate free radicals:

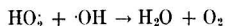
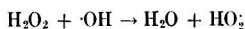
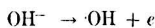


Their excess oxygen was closely accounted for quantitatively by measuring the chlorine dioxide and chloric acid and calculating the excess oxygen from the above equations. Their ozone current efficiency was small at this high acid concentration.

Boelter (20) showed that chlorine dioxide is also formed in detectable amounts in 2M perchloric acid at 10 amp/cm². He detected chlorine dioxide as did Grube and Mayer by absorbing the anode gas in ferrous ion solution and titrating the chloride ion formed with silver nitrate. His points of initial detection of chlorine dioxide occurred at currents greater than ten times the limiting current density in 2-11M perchloric acid at 0°C. No change is observed in the slope of the overvoltage curve at the point where chlorine dioxide is first detected.

Oxygen formation.—Ozone and chlorine dioxide were not detected below the region of the limiting current density. In fact, no substance was present in the electrolyte below the region of the limiting current density in any concentrated perchloric acid that could be detected idometrically with a sample of the electrolyte after electrolysis. Therefore, it is concluded that oxygen is the only anode product liberated.

Hickling (21) has suggested the following mechanism for oxygen formation in basic solution:



In acid solution the first step would be



This is the only step for which a lower activity of water would reduce the reaction rate.

DISCUSSION

The limiting current density and overvoltage rise can best be explained by adsorption of perchlorate ions. The following mechanism is postulated:

1. Perchlorate ions are adsorbed on the anode due to a combination of adsorption forces and coulombic attraction to the positively charged anode. They either displace or adsorb on the already existing monolayer of oxygen.

2. Oxygen formation reactions are crowded onto sites unoccupied by perchlorate ions. Therefore, the actual current density at a given apparent current density increases and this increases the overvoltage.

3. Overvoltage increases until perchlorate ions discharge. Discharge of perchlorate ions results in the upper Tafel line.

Decrease in the limiting current density in increased perchloric acid concentration is to be expected for an adsorption mechanism. A plot of the logarithm of the limiting current density from Fig. 5 vs. the logarithm of perchloric acid activity yields a straight line. For convenience the limiting current density was arbitrarily taken as the midpoint of the curve connecting the upper and lower Tafel lines. Perchloric acid activity was calculated from the data of Robinson and Baker (14). There is no such relation of the limiting current density to the activity of water. The limiting current density continues to increase with dilution, but the water activity reaches a limiting value of unity. It appears then that interaction of perchlorate ion rather than a slow reaction involving water is the cause of the limiting current density.

The decrease in the limiting current density at low temperatures is also in accord with the adsorption mechanism. Lower temperature favors physical adsorption in general, and the increase in oxygen overvoltage at low temperature favors coulombic attraction. The slow approach to steady-state potentials in the region of the limiting current density is also in accord with the general slow attainment of adsorption equilibrium.

The point of inflection of the curve connecting the upper and lower Tafel lines is assumed to represent the point where perchlorate ion discharge begins. This is in accord with the detection of chlorine dioxide on the upper Tafel line where there is no further change in slope. The first perchlorate ions to discharge are evidently reacted to form HClO₃ and oxygen by a mechanism similar to that postulated by Grube and Mayer (19), but, as the current density is increased, chlorine dioxide is formed at a sufficient rate to escape from the solution.

The ozone produced in the region of the limiting current density and the ozone produced in high concentration at high current density can be explained by two different mechanisms. The first is probably produced by discharge of water by a similar mechanism to oxygen formation and the formation of ozone by electrolysis of concentrated potassium hydroxide solutions at low temperature (22). The initial increase in overvoltage provides the energy for this reaction. The rate of ozone formation becomes constant or decreases when perchlorate ion discharge begins, thus resulting in a maximum in concentration. The high concentration ozone at high current density could be explained by a reaction involving perchlorate free radicals. This is analogous to the formation of ozone by heating persulfates in sulfuric acid reported by Ulrich (23).

The above theory explains qualitatively all of the experimental facts. Data for other electrolyte systems will be presented in another paper.

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The Anode Behavior of Germanium in Aqueous Solutions

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ABSTRACT

The anode characteristics of *n*- and *p*-type germanium are different. A large voltage barrier is observed at about 0.8 ma/cm² current density at room temperature on *n*-type but not on *p*-type electrodes. The voltage barrier on 3 ohm-cm *n*-type germanium anodes breaks down at about 9 volts in many electrolytes. During anodic dissolution the germanium surface appears to be covered with about a monolayer of oxide or hydroxide. This suggests that germanium goes into solution as a complex ion with the hydroxyl or oxide radicals attached. A mechanism is proposed for the over-all anode dissolution process involving two holes and two electrons for each germanium atom dissolving.

INTRODUCTION

The relatively small number of current carriers in semiconductors such as germanium make them poor conductors of electricity as compared to most metals. This low carrier density and the fact that current may be carried by both electrons and holes has an effect on the electrolytic behavior of germanium in electrolytes since it is possible to produce appreciable carrier concentration gradients inside the semiconductor at moderate current densities.

The semiconductor physics of *n*- and *p*-type germanium as anode and cathode in electrolytes has been investigated by Brattain and Garrett (1, 2). By changing the relative concentration of holes and electrons in the germanium surface with light, they have shown that the rate of the anodic dissolution process is controlled by the supply of holes at the germanium-electrolyte interface. The observed potential of a germanium anode therefore may be composed of three parts: (a) the reversible potential of germanium in the electrolyte; (b) the polarization po-

tential which is given by the Tafel equation; and (c) an internal space charge potential due to a concentration gradient of holes just under the germanium surface. The latter is significant only when holes are the minority carrier, i.e., when the germanium is *n*-type.

The anodic solution of germanium has been studied by Jirsa in acid and alkaline solutions (3). He reports that germanates are formed in alkaline solutions while the corresponding germanium salts are formed in acid electrolytes. There is good evidence, however, which indicates that the stable form of germanium in acid solutions is metagermanic acid, H₂GeO₃ (4).

The purpose of this investigation was to learn something of the nature of the electrode reactions occurring at a germanium anode in aqueous solutions.

EXPERIMENTAL

Two methods were used to study the anode behavior of germanium: (a) the electrode potential was measured relative to a saturated calomel reference electrode at various current densities; and (b) electrode potential

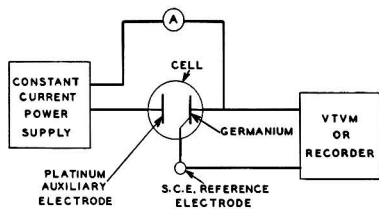


FIG. 1. Experimental arrangement for dynamic potential studies.

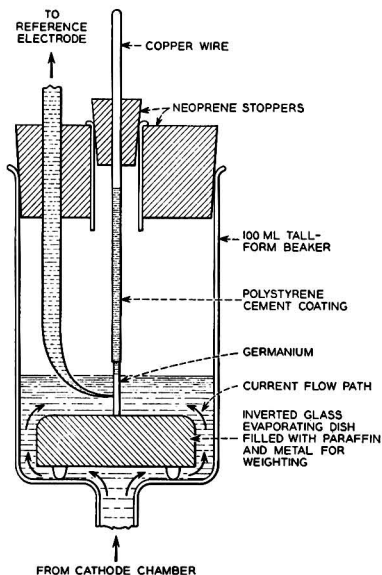


FIG. 2. Cross-section view of the anode chamber designed for uniform current distribution.

changes with time were recorded while a constant current was started, stopped, or reversed through the electrolytic cell.

The experimental arrangement is shown schematically in Fig. 1. Voltages up to 1.4 v were measured with a Leeds and Northrup pH indicator meter. A General Radio Type 728-A d-c vacuum tube voltmeter was used for higher voltage measurements. Potential-time curves were recorded on a Model 127 Sanborn recorder. The electrolytic cell was designed so that current distribution over the germanium electrode was uniform, see Fig. 2. The tip of the Luggin capillary was positioned so that only one corner touched the germanium electrode. This arrangement produces a negligible amount of masking by the capillary tip and yet insures sufficient proximity to avoid including an appreciable solution IR drop in the potential measurement. A constant current power source consisted of 180 v (large dry cell batteries) in series with a large resistance. A platinum electrode 1 cm² area was used as the auxiliary electrode. Single-crystal germanium bars 2 mm x 1 mm in cross section and lengths of about 1 cm for p -type and 2 cm for n -type were used as electrodes. These were soldered with appropriately doped lead-tin

solder to 50 mil diameter copper wires for support and an ohmic electrical connection. The solder joint and an area above and below were coated with polystyrene cement. Electrodes usually were immersed up to the edge of the polystyrene coating. The resistivity of both types of germanium was about 3 ohm-cm.

Solutions of 0.1N sulfuric acid and 1N potassium hydroxide either initially free of germanium or saturated with germanium dioxide were used for most of the experiments. The most reproducible data were obtained with electrolytes saturated with germanium dioxide.

Electrode Potential-Current Characteristics

The primary anode reaction at a germanium electrode in aqueous solutions is germanium dissolution. At low current densities, anodes of both n - and p -type germanium obey the Tafel equation: $E = a + b \log i$, where E is the anode polarization potential, i is the current density, and a and b are constants. In 0.1N sulfuric acid, the slope b is 0.12 which is about the value usually observed. Deviations from the Tafel relation occur with both germanium types, but the greatest change takes place with n -type electrodes as shown in Fig. 3. The large rise in potential in the vicinity of 0.8 ma/cm² current density is similar to the current block obtained with solid-state rectifiers. The value of 0.8 ma/cm² cannot be considered too significant, since the saturation current density is a function of the resistivity and the minority carrier lifetime of the germanium used as anode. Uhler (5) has found that the temperature variation of the saturation current of the barrier between n -type germanium and potassium hydroxide solution is quite like that of a p - n junction. About a tenfold increase in the saturation current is obtained for each 30°C rise in temperature. The anode potential in the saturation current region is also photosensitive (6). Light furnishes hole-electron pairs at the surface which tend to destroy the voltage barrier. All electrode potential-current measurements were made with the germanium electrode under study in the dark. The saturation current observed on n -type germanium anodes has been shown by Garrett and Brattain (2) to be due to a depletion of holes at the anode surface. Since holes are the minority carrier in n -type germanium, the saturation current repre-

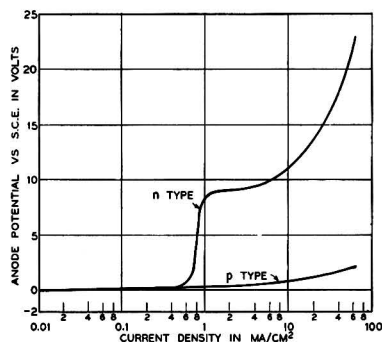


FIG. 3. Typical anode potential-current density curves for n - and p -type germanium in 0.1N H₂SO₄ saturated with GeO₂. Temp. \approx 25°C; electrode in dark.

sents the point at which holes are used up in the anode process as fast as they are able to diffuse in the germanium from the bulk to the surface.

The anode voltage barrier on *n*-type germanium breaks down at about 9 v in 0.1*N* sulfuric acid as shown in Fig. 3. The breakdown potential should be a function of the resistivity of the germanium (7). The higher the resistivity the greater the breakdown voltage. There is a tendency for the anode potential to continue up without a breakdown under some conditions. This always occurs in concentrated salt solutions of sodium dichromate or sodium nitrate. When breakdown does occur even in these electrolytes, however, the anode potential never falls below about 9 v. The breakdown in the voltage barrier is assumed to be an avalanche type of breakdown (7). Hole-electron pairs are produced in the breakdown process and the anode current is no longer controlled entirely by the diffusion of holes from the germanium bulk. *n*-Type germanium electrodes were always pitted after being made anode above the breakdown potential. It is believed that breakdown only occurs at these points of pitting and the reason breakdown may not take place in concentrated electrolytes is that any pits which form become filled with anodic products which are not readily soluble in the electrolyte. This may also explain the rapid rise in potential at high current densities in 0.1*N* sulfuric acid as shown in Fig. 3.

The anode efficiency of germanium dissolution was measured in a 1*N* potassium hydroxide electrolyte at current densities ranging from 3.5 to 50 ma/cm² using a copper coulometer. Assuming a germanium valence of four, the anode efficiencies were remarkably uniform at about 95%.

The relatively small deviation in the anode potential of *p*-type germanium from the Tafel equation at high current densities can be attributed to two *IR* drops, one in the germanium and the other in an anode film of germanium dioxide which forms faster than it can be dissolved by the electrolyte. The *IR* drop in the germanium electrode at the highest current was less than 0.2 v which accounts for only a portion of the deviation.

Oscillographic Studies of Germanium Surfaces

The nature of the surface of germanium after a chemical or electrochemical treatment may be studied by either reducing or oxidizing the surface layer electrochemically. The technique involves starting, stopping, or reversing a constant current through the cell while the electrode potential against a saturated calomel reference electrode is recorded on an oscillograph. These potential-time records may be used to determine the number of coulombs required to carry out a particular electrochemical reaction and thus the amount of material involved in the process. The potentials themselves are characteristic of the materials taking part in a particular electrode process. This technique has been used in the study of tarnish films (8).

A typical oscillograph record with germanium electrodes made anode and cathode in 0.1*N* sulfuric acid is shown in Fig. 4. The record begins with the open circuit (zero current) electrode potential and then successively the germanium is made anode, cathode, and anode again.

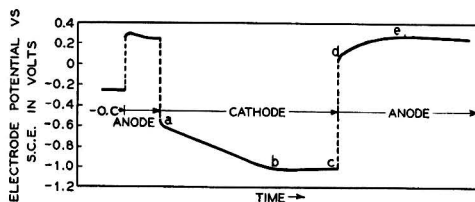


Fig. 4. Typical oscillograph record of germanium made anode and cathode in 0.1*N* H₂SO₄; current density \approx 0.3 ma/cm².

When germanium is made anode in solutions there always is some "overshoot" in potential. The term "overshoot" is applied to the initial maximum observed in potential-time curves and is often observed for other metals. In oxidizing solutions such as chromic acid this can be a very large effect on germanium amounting to several volts. The actual amount of overshoot voltage obtained appears to be a logarithmic function of the constant current applied to the cell. Oxidizing solutions appear to form a protective oxide layer on germanium which inhibits the anodic dissolution process. This causes the electrode potential to rise above the normal dissolution potential for the applied current. As the protective film is removed by being physically displaced or undermined, the anode potential drops to the stable value. The steady-state anode reaction is germanium dissolution. A discussion of this process will be given later.

When the electrode is switched from anode to cathode (by reversing the cell current) in Fig. 4, the potential changes abruptly to *a*. The potential at *a* is about -0.65 v vs. S.C.E. or -0.4 v on the hydrogen scale. The standard electrochemical potential of germanium is believed to be about the same value. This is followed by a relatively slow linear increase in the cathode potential with time along *ab*. At *b* the electrode potential reaches a stable value. The cathode reduction process *ab* always requires about 4×10^{-4} coulomb/cm² regardless of the cathode current density or the anodic pretreatment time or current. This is significant since it means that in the continuous anode dissolution process the germanium surface layer always contains a definite amount of reducible material. These results will be considered in discussing the anode and cathode processes. The final cathode reaction *bc* is the discharge of hydrogen ions and evolution of visible hydrogen gas. The cathode potential at *b* increases in proportion to the log of the current density. This also results in a slight increase in the length of section *ab* and is attributed to the coulombs required to charge the electrical double layer capacity (about $20 \mu\text{F}/\text{cm}^2$) to the higher cathode potential. The anode curve obtained when the germanium electrode is switched from cathode to anode has an approximately linear section *de* which involves about 2×10^{-4} coulombs/cm² or half of that used in the cathode process *ab*.

DISCUSSION

The voltage barrier observed when *n*-type germanium is made anode at a critical current density has been at-

tributed to a p - n junction at the surface (2, 9). A layer of negative charges attracted to the surface by the anode bias induces in the surface of the germanium a thin layer which is changed from n - to p -type. This p -type surface layer next to the n -type bulk germanium makes a p - n junction and the voltage bias is in the blocking direction. No anode voltage barrier is found with p -type germanium since the anodic surface condition described only tends to make the germanium surface layer more p -type than the bulk.

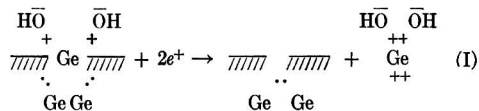
The critical current at which blocking begins on n -type germanium when made anode in an electrolyte is determined by the rate at which electrons are extracted from the solution into the germanium and/or holes diffuse from the germanium bulk to the surface. Electrons can be extracted from solutions only by anion discharge. Hydroxyl ions are the most easily discharged anions in the solution studied. No oxygen gas bubbles were visible at the anode, however, to indicate hydroxyl ion discharge. Furthermore, anode efficiency measurements show that the sole anode process at the point of current saturation is germanium dissolution. Thus, saturation current appears to be controlled only by the rate of hole diffusion. In order to put a germanium ion into solution from a site on the surface of a crystal lattice, chemical bonds to underlying germanium atoms must be broken. The process requiring the least amount of energy to break these bonds is the migration of holes from the germanium bulk to the surface. Below the breakdown potential these holes come largely from the bulk. Above breakdown, the migrating holes multiply in the high field of the space charge region at the surface to increase germanium dissolution and the flow of current through the electrolysis cell.

A breakdown in the voltage barrier would also occur if the potential at the germanium-solution interface were to exceed that required for the continual discharge of anions (10). As previously stated, however, no anion discharge was observed.

The electrochemistry of the steady-state anode reaction at germanium electrodes in sulfuric acid below the saturation current for n -type was studied with the aid of cathodic reduction experiments. The observed linear change in cathode potential with time at a constant current after an anodic pretreatment is the type of curve expected where the material being reduced is present initially as a monolayer or less. The cathode potential increases as the surface area covered with the material being reduced decreases. As the concentration of the reducible material approaches zero, the cathode potential becomes relatively constant and corresponds to the polarization voltage of hydrogen ion discharge on germanium.

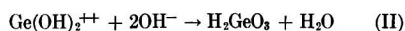
A mechanism of germanium dissolution was suggested by the results of the anode-cathode curves in 0.1*N* sulfuric acid. The 4×10^{-4} coulombs/cm² required in the cathode reduction process turns out to be about 4 electrons per surface germanium atom, assuming that the true area of a chemically polished surface is about 1.4 times the apparent area (11) and the surface atoms are arranged according to a (100) crystal orientation. Since the same amount of material is cathodically reduced regardless of the anodic pretreatment time or current density, the

germanium surface layer must contain a fixed amount of reducible substance continuously during the anode process. This result can be explained if it is assumed that the surface layer always contains about a monolayer of hydroxide or oxide during germanium dissolution. Since free Ge⁺⁺ germanium ions do not exist in aqueous solutions to any extent, it is likely that germanium ions go into solution as complex ions with the hydroxide or oxide radicals attached. This anode process may be shown schematically as follows:

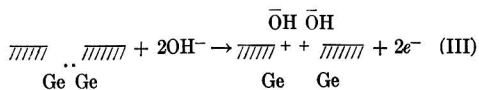


(The dots represent covalent bonding electrons and e^+ represents a hole.)

The electrochemical reaction written suggests that in the anodic process the covalent bonds between a surface germanium and underlying atoms are broken by the arrival of two holes. It has been shown that holes are required to carry out the primary anode process on germanium (2). As the germanium ion enters the solution, it reacts chemically with hydroxyl ions. In neutral or acid solutions, metagermanic acid is formed:



It was stated previously that hydroxyl ions did not discharge to form visible oxygen gas on germanium anodes in the electrolytes used. It is believed, however, that hydroxyl ions react with clean surface germanium atoms to the extent that a monolayer of hydroxide or oxide is maintained, as follows:



The over-all germanium anode reaction in aqueous solutions is, therefore:

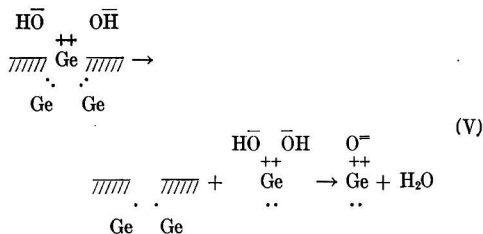


The four electronic charges required to dissolve one germanium atom are conducted away from the surface as two holes and two electrons. This is consistent with the results of Garrett and Brattain (2) who found that when holes were injected into an n -type germanium anode, the anode current changed about twice that of the injected hole current.

Above the breakdown potential, about 9 v in 0.1*N* sulfuric acid, it is assumed that holes also become available at the surface as the result of the creation of hole-electron pairs in the space charge region by the avalanche process, and the kinetics of the germanium dissolution process is no longer limited by hole diffusion from the bulk.

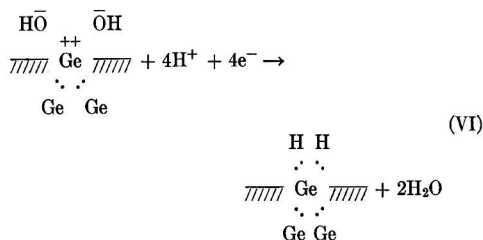
At very high current densities germanium may go into solution so rapidly that the electrolyte cannot dissolve it all and white GeO₂ forms on the surface. Occasionally an orange colored deposit is observed on germanium after being anodized at high current densities. This has been

identified as the germanium monoxide (3). The effective valence for germanium dissolution under these conditions is two. The primary reaction may be as follows:



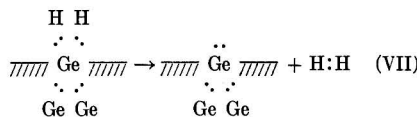
The two electrons are obtained in returning the monolayer of hydroxide to the surface, equation (III).

The initial reaction proposed when a germanium electrode is switched from anode to cathode, i.e., when the current is reversed in the electrolytic cell, is the reduction of the hydroxide or oxide surface layer and the formation of a hydride layer as follows:

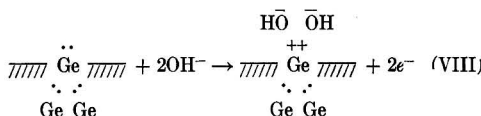


This is the electrochemical process which was observed experimentally and required about 4×10^{-4} coulomb/cm² or four electrons for each surface germanium atom. The initial assumption about the nature of the germanium anode surface is based on these results.

When germanium is made anode immediately after being cathode, only two electrons per surface germanium atom were required in the initial oxidation process. This result can be explained if it is assumed that the hydrogen atoms of the surface hydride prefer to combine chemically as molecular hydrogen rather than be oxidized back to hydrogen ions when the current is reversed:



This chemical process may then be followed by the electrochemical reaction:



where two electrons are required for each surface germanium atom to return it to the condition of anode dissolution.

SUMMARY AND CONCLUSIONS

1. The primary anode reaction at a germanium electrode is germanium dissolution. The *E-I* curve obtained for a germanium anode in aqueous solutions is different for *n*- and *p*-type germanium. A surface barrier is observed with 3 ohm-cm *n*-type germanium electrodes at room temperature at about 0.8 ma/cm² current density. The voltage barrier which is attributed to a limiting rate of hole diffusion to the surface breaks down at about 9 v. The breakdown is presumed to be similar to the avalanche type of breakdown which occurs in solid-state *p-n* junctions.

Deviations from the Tafel equation with *p*-type germanium at high anode current densities are attributed to *IR* drops in the bulk of the electrode and an anode film of germanium dioxide.

2. When germanium is made anode in aqueous solutions, the anode potential-time curve passes through an initial maximum which signifies that germanium has some difficulty in dissolving at first. This is attributed to a protective oxide layer on the surface which inhibits dissolution until it is removed by some displacement process. The effect is very large in strongly oxidizing solutions such as chromic acid where the oxide layer is more protective against anodic dissolution.

3. The results of the anode-cathode potential-time curves indicate that during anodic dissolution the germanium surface is always covered with a monolayer of hydroxide or oxide. It is suggested that germanium goes into solution as a complex ion with the hydroxide or oxide radicals attached. The mechanism proposed for germanium anode dissolution is a two stage process: (a) the germanium complex ion goes into solution when two holes arrive at the surface, and (b) two hydroxyl ions react with the surface giving up to conducting electrons to the germanium and renewing the surface monolayer of hydroxide or oxide.

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Etching Silver with Chromium Trioxide-Sulfuric Acid Solution

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The purpose of the etching process described in this paper is to clean and alter the surface of silver to provide a substrate suitable for subsequent surface treatment. A comparable conditioning procedure, for example, is the etching of aluminum foil for electrolytic capacitors to clean and roughen its surface in order to increase the capacitance per unit of superficial area. The process for surface-conditioning silver can be made essentially continuous and is carried out at room temperature with a dilute aqueous solution of chromium trioxide and sulfuric acid.

Neither of these substances alone in dilute aqueous solution attacks silver at room temperature. Boiling 2% aqueous sulfuric acid solution shows virtually no attack on a silver surface and boiling 2% aqueous chromium trioxide produces only a slight etch on a silver surface immersed for 2 min in the solution.

However, if the two substances are present simultaneously in one solution, their combined action on silver is evident at once. For example, if a strip of silver foil 0.5 mil to 1 mil in thickness is suspended in a boiling solution containing 2% by weight CrO_3 and 1% by volume of H_2SO_4 , sp gr 1.84, the solution attacks the silver so rapidly that the foil is completely dissolved in about 5–10 sec.

At room temperature the attack of the chromium trioxide-sulfuric acid solution on silver is much more moderate than at about 100°C where rapid dissolution of the foil occurs. Exposure of the silver to the etching solu-

tion at room temperature for 15 or 30 sec produced fairly well-etched surfaces. A 1-min immersion of the foil gave a good etch, and a 2-min exposure an excellent etch. A 4-min immersion caused slightly more loss of thickness than was desirable. Eight-minute and 12-min immersions caused further loss in thickness but no noticeable erosion or cavitation at the edges of 1-mil foil. A 16-min immersion reduced 1-mil foil to less than one-half its original thickness and showed evidence of preferential erosion at the edges of the specimen.

A 1- to 2-min immersion was estimated to be sufficient to produce an etched surface of the type desired without sacrificing too much of the original thickness of the material.

About 125 ft² of silver surface in the form of 1-mil foil, 3 in. wide could be etched satisfactorily with the following solution:

Chromium trioxide	40 g
Sulfuric acid (sp gr 1.84)	20 cc
Water	2000 cc

A coating of red-brown material, presumably silver dichromate, remains on the silver as it is drawn from the etching bath. However, this coating is not very adherent and is rinsed off readily with water sprays directed against both sides of the strip of foil.

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Energy Losses from Furnaces and the Concept of Efficiency Implications for Furnace Design and Operation

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INTRODUCTION

To succeed in any line of human endeavor it is necessary to have reliable criteria of success to apply to the intermediate operations that lead to the final result. In particular, furnaces are normally operated for eventual profit, and reliable criteria are needed to determine when operations are economical. The criterion most commonly used for this purpose is efficiency. The following text exposes some weaknesses of this usage, and suggests a systematic procedure by which these weaknesses can be eliminated.

The terms "energy balance" and "heat balance" are also used as criteria of performance, and it is shown here that they frequently lead to very much the same difficulties as the concept of efficiency.

Both efficiency and energy balance can be defined simply. However, these concepts are tools, and frequently these tools are not flexible enough to do the job at hand. The basic relationships that underlie the definitions merit serious consideration. Such consideration will lead to better design and more economical operation of equipment.

This paper points out the limitations of the usual concepts, and shows how to classify in a concrete and useful way the various mechanisms by which energy is either used profitably or lost.

CONCEPT OF EFFICIENCY

The term "efficiency" is widely used in technical literature. Sometimes it means "yield" as in the useful expression "kwhr/lb of product." However, this use of the word is misleading, especially in furnace operation where it is easily confused with "energy efficiency." A better term would be "specific yield." In the following text the word efficiency will be used only in the sense of the following definition:—

Efficiency = useful energy/total energy consumption

This is a simple expression and in many cases it is a useful one. However, it has limitations when used in real situations, as will be shown.

The concept of efficiency is used to compare the economic utility of two or more furnace operations. This comparison may involve different furnaces of the same type, furnaces of different types, or the same furnace at different times. The various combinations are obvious. For example, two arc furnaces may be compared for a given smelting operation, or an arc furnace can be compared with an induction furnace.

The engineer must make these comparisons by the best means at hand. The concept of efficiency was used in analyzing mechanical apparatus, motors, and power generating equipment long before it was applied to furnaces. It has been used in furnace work, but examples to follow will show that the disarming simplicity of the original idea has been carried over to furnace practice without sufficiently critical examination and with resulting difficulties.

Note, for example, that it is meaningless to say that a given furnace has a certain specified efficiency unless it is also specified (a) whether or not the furnace is fully loaded, (b) what process is being carried out, (c) the operating schedule, and (d) the functioning of any auxiliary equipment. More specific examples follow.

Consider a simple resistance-type furnace used for heat treating, and assume that the wall losses are constant at 20 kw. The maximum available power is 200 kw, but the power input is adjusted to the size of the load to maintain a constant heating rate. When the furnace is fully loaded, the full power of 200 kw can be applied, and all but the 20 kw wall losses is useful energy. The efficiency is then $180/200 = 0.90$. Assume an extreme case in which the furnace is operated at one-tenth of its full-load value, or 18 kw. However, the wall losses remain at 20 kw, so the total input must become 38 kw, an efficiency of 0.47. The efficiency is, therefore, a function of furnace load.

Consider an arc furnace for steel production. Since constant temperature is maintained during the refining period, no useful heat is consumed in this period. Depending on end requirements, the refining period may vary from one to three hours, showing a large variation in efficiency. The efficiency in this case is a function of the operating schedule.

The experienced furnace man will realize without further examples that an efficiency figure becomes meaningful only when hedged in by a number of restrictions that make it quite unwieldy. The result is that the true efficiency of a furnace can be recorded and studied only by compiling a large volume of data that can be grasped in entirety only by considerable effort.

HEAT BALANCES

Heat balances avoid some of the objections raised against the use of "efficiency." This comes about because it is not necessary to label heat "useful" or "lost." The competent engineer will know at once which portions of the energy consumed are useful for his particular purpose,

TABLE I. *Energy balance of arc furnace in per cent*

<i>Input</i>	
Electrical energy	84
Heat of reaction	9
Heat produced by oxidation of electrodes	7
	100
<i>Energy expenditures</i>	
Temperature increase of steel	42
Temperature increase of slag	8
Wall losses by surface radiation	17
Wall losses by water cooling	13
Losses from escaping gases	4
Electrical losses	16
	100

TABLE II. *Energy balance of arc furnace in kwhr*

<i>Input</i>	
Electrical energy	5460
Heat of reaction	585
Heat produced by oxidation of electrodes	455
	6500
<i>Energy expenditures</i>	
Temperature increase of steel	2730
Temperature increase of slag	520
Wall losses by surface radiation	1105
Wall losses by water cooling	845
Losses from escaping gases	260
Electrical losses	1040
	6500

and he avoids having to use troublesome and largely unnecessary labels. As long as he knows where the energy is going he has all the necessary information. However, the following example will show that heat balances also can prove to be pitfalls for the unwary.

Consider an arc furnace used for melting steel. Table I gives an energy balance in percentages of the total. However, this tabulation is quite inflexible. Note that if any item, such as load or electrode diameter, is changed, all the percentages will have to be changed to make the totals come out to 100%.

The above situation can be improved somewhat by writing a new balance in kilowatt hours, assuming that the total energy required for a heat is 6500 kwhr. This is done in Table II.

However, the simplicity of this tabulation can be misleading. Consider what happens if the load is increased somewhat and the heat required by the steel and slag increase by 10%, to 3003 and 572 kwhr, respectively. If these increased figures are merely written in the place of the old ones in Table II, the assumption is being made that the other energy expenditures remain unchanged. This assumption is not true. Power input and/or time of heating must be increased. Either one increases electrical losses, and longer time of heating results in increased wall losses. The conclusion is that a 10% change in load makes an entirely new heat balance necessary. This is essentially the same difficulty encountered in the use of "efficiency" as a criterion of effectiveness.

The foregoing text has shown that the traditional ways of analyzing furnace operations frequently lead to undesirable complexities. The remainder of this paper

explores a new method of classifying energy expenditures with a view to making the analysis simpler and less ambiguous.

GROSS USEFUL HEAT

Before developing the proposed new method of classifying energy expenditures, a definition is necessary. First, the total energy input to the furnace will be considered to comprise two components: (a) gross useful heat, and (b) losses. Gross useful heat then consists of any energy increase, as expressed in temperature rise and increased latent heat content, of material not permanently in the furnace. Thus, it includes energy stored in containers and in means of conveyance in heat treating furnaces, heat stored in metal as well as in slag in melting furnaces, etc. Note that this definition is unambiguous, since the permanent parts of the furnace are clearly and easily distinguishable from the materials and equipment that pass in and out of the furnace in operation.

Losses are defined as the difference between total energy input and gross useful heat.

CLASSIFICATION OF LOSSES

The classification of energy losses is the essential feature of the point of view described in this paper. Note that any specified loss may or may not be proportional to gross useful heat. It also may or may not depend on other losses. Losses are, therefore, divided into the following four classifications:

- (a) Proportional dependent
- (b) Proportional independent
- (c) Nonproportional dependent
- (d) Nonproportional independent

This system of classification involves one slight complication that must be faced at the outset. An example will make it clear. Consider the sum of the ohmic losses in electrodes, bus bars, transformer, and reactor of an electric furnace. This ohmic loss is generally proportional to total power input into the furnace proper, which input depends both on gross useful heat and on other losses, e.g., wall losses from the furnace shell. These electric losses therefore comprise two parts, one proportional independent and the other nonproportional dependent.

Such losses will be classified as "proportional dependent." In general they will not be simultaneously proportional and dependent, as perhaps implied by the literal meaning of the words. In this context, the term will be used to denote such losses as comprise two parts, one proportional to gross useful heat and the other dependent on other losses.

To render the above classification more concrete, a number of examples of losses will be given. At this point it is convenient to start with the simplest classification, nonproportional independent.

The most important examples of nonproportional independent losses are wall losses in furnaces and core losses in transformers.

An interesting example of proportional independent losses occurs in heat treating a stack of bars where part of the stack protrudes from the furnace. Heating of the

protruding ends, while unavoidable, is not necessary, and constitutes a loss that is proportional to gross useful heat and independent of other losses.

Other examples of proportional independent losses are part of the ohmic losses in electrodes, busses, etc., as already noted, and part of the coil losses in induction furnaces.

Nonproportional dependent losses are widespread. For example, the losses mentioned in the preceding paragraph have a component in this category.

Some of the advantages obtained by analyzing energy expenditures in this way are illustrated by the following examples.

Furnaces that are expected to undergo extended periods of operation at reduced output call for extreme care in reducing nonproportional losses, even, if necessary, at the expense of proportional ones. This procedure may in some cases even result in higher power consumption at full load, but will reduce power consumption during the periods of limited output.

The electrical efficiency of induction heating equipment is frequently only 50%. Only 50% of the electrical input to the generator finds its way into the charge as heat. Part of this heat is lost by radiation from the crucible. This energy lost by radiation has first to be transferred (in the form of electrical energy) from the coil to the charge. Assume a specific case in which thermal insulation would reduce the radiation by 2 kw or 6800 BTU/hr. To get this 2 kw, which can be saved, into the work requires the expenditure of 4 kw of electrical energy at the input of the generator. The cost of the insulation should then be compared with the saving, not of 2 kw, but of 4 kw.

Consider a furnace for which conditions have been well established and assume that the operating schedule has to be changed. If the operator has analyzed the past operation of the furnace in the way recommended in this paper, he will immediately know whether the operating data being obtained under the newly established conditions are normal or indicate a need for further adjustment of the operating parameters. These considerations are especially true when furnaces must be run at reduced output, since the danger of uneconomical operation is usually increased at such times.

In general, a close analysis of losses and the relationships between them will enable the operator to make maximum use of the data already recorded in predicting the results to be expected under changed conditions.

ALGEBRAIC ANALYSIS

It would be highly advantageous to reduce the recommended procedures to a series of algebraic operations that would yield the desired information almost automatically. While this objective can probably be attained in some cases, it is not attainable in general. However, a start has been made in this direction and is outlined below.

Consider the total energy q required for a process. The gross useful heat is u and the sum of the nonproportional

independent losses is NI . These figures represent energy per batch or cycle for a cyclic operation or per hour for a continuous operation. Then,

$$q = \frac{u(1 + P) + NI}{D} \quad (I)$$

where P and D are defined as follows: P is defined by the postulate that Pu is the sum of all proportional independent losses. P is then the sum of P_1, P_2, P_3 , etc. Each P_i represents for one kind of proportional independent loss the ratio "loss/gross useful heat." The value of P is not limited, and it will exceed one if proportional losses are larger than gross useful heat.

D is defined by equation (I) above, which can be rewritten as follows:

$$D = \frac{u(1 + P) + NI}{q} \quad (II)$$

Note the resemblance to the equation defining the "thermal efficiency" E ,

$$E = \frac{u}{q} \quad (III)$$

D therefore bears a family resemblance to E , but permits the proportional independent losses Pu and the nonproportional independent losses NI to appear explicitly in equation (I).

In combustion furnaces, D might conveniently be called "efficiency of combustion" and defined as:

$$\frac{\text{Heat content of fuel} - (\text{stack losses} + \text{losses from incomplete combustion})}{\text{Heat content of fuel}}$$

In induction heating, D might be called electrical efficiency and defined as:

$$\frac{\text{Power input} - \text{ohmic losses in the coil}}{\text{Power input}}$$

CONCLUSION

The classification of losses by the method outlined in this paper is recommended to the designer and operator of furnaces as a new analytical tool. In general, these procedures will be less simple than older methods, but the effort required will be rewarded by more economical furnace design and operation.

ACKNOWLEDGMENT

G. H. Fetterley, to whom the author is very grateful, engaged in a thorough discussion of a number of points raised in this paper.

Manuscript received April 7, 1955. This paper was prepared for delivery before the New York Meeting, April 12 to 16, 1953.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1956 JOURNAL.

Monsanto Chemical Co.—ECS Sustaining Member



Aerial view of Monsanto Chemical Co.'s electric furnace elemental phosphorus plant at Monsanto, Tenn.

From one product and a single plant in St. Louis in 1901, the Monsanto Chemical Co. has grown to be one of the five largest general line chemical companies in the United States.

The one product and the one plant now have grown into hundreds of products flowing from 24 plants in the U. S. and from another dozen plants located in all parts of the world.

The 55-year growth pattern, which might at first seem unusual, actually is just about par for the course in this age which is frequently called the "Chemical Century."

Cutthroat competition by the German chemical trust cost the company several losing years before it finally turned its first profit of \$10,600 in 1905. In 1917, Monsanto really started on the growth trail with the purchase of the Commercial Acid Co. near East St. Louis, Ill. An unfavorable British tariff in 1920 prompted Monsanto's first expansion into the foreign field with the purchase of a half interest in the Graesser Chemical Co. at Ruabon Wales, first unit of the future Monsanto Chemicals Ltd. The other half interest was bought in 1928.

In ensuing years, other chemical lines were acquired, further broadening the efforts of the company. A major expansion in phosphates—and in the electrochemical field—came in 1935. The Swann Corp., with its plants at Anniston, Ala., Carondelet, Mo., and Camden, N. J., merged with Monsanto.

Phosphate production soared after construction the following year of a plant at Monsanto, Tenn., for large-scale recovery of elemental phosphorus through the electric furnace process. Continuous expansion in this particular field, with six furnaces now at Monsanto, Tenn., and another two furnaces at Monsanto, Idaho, have retained the title for the company of the world's largest producer of elemental phosphorus.

The achievements in the phosphate field were recognized in 1937 with the award to Monsanto of the Chemical Engineering Achievement Award for "successfully developing the large-scale production of elemental phosphorus in such a way as to open up an entirely new field for the chemical industry."

Other broadening acquisitions in the intervening years, climaxed by the merger with Lion Oil Co. just last year, have now brought Monsanto past the half-billion dollar mark in annual sales. The interest ranges from synthetic fibers to synthetic detergents, and from fine chemicals for foods to heavy acids for industry.

The basic chemical reaction underlying Monsanto's production of high quality elemental phosphorus is the intra-reaction of phosphate rock, coke, and silica sand. The reaction requires a temperature of 1300°–1500°C to start. When this heat is obtained, the coke reduces the free phosphorus pentoxide to elemental phosphorus vapor; the silica sand combines with the resulting lime to form a slag.

Yellow phosphorus is condensed from the top of the reaction chamber and a molten slag is tapped off the furnace at the bottom. As the slag spills out down directed run-out troughs, a compound of iron and phosphorus, ferrophosphorus, separates out. This iron-phosphorus is the steel industry's principal source of phosphorus for special steels.

Although Monsanto's original furnaces had rated capacities of 8000 kva, the last four installed furnaces had rated capacities of more than three times that. And all of the furnaces have since undergone technical improvements which have further raised their consumption of electric power and also their output. The electric consumption in the Tennessee plant alone is far more than, for example, that used by the city of Memphis.

In the searing heat and blinding light of giant carbon arcs, one of the earth's most tightly bound servants is set free for man's use, to become the starting point of hundreds of industries, thousands of products, and an uncountable number of uses, many of which today are still to become known.

But the distilling and condensing is not the end. Another whole technology, pioneered by Monsanto, is bound up in the handling and transportation of this fickle element. Contact with air—and the docile servant becomes a burning demon. Hence from the condensing units, phosphorus is pumped as a liquid in water-jacketed pipes to storage tanks. Tank cars carrying the element to distant locations for further processing are capped with a blanket of water to keep the fiery demon docile.

Industries served by phosphorus and phosphates include textile dyeing, cloth processing, ceramics, detergents, oil drilling, pharmaceuticals, fiber bleaching and processing, leather tanning, and many others. No list could be made large enough to enumerate all the products using phosphates directly in their manufacture. If such a list were possible, it would still be a small fraction of the uses to which phosphorus or phosphates are contributing chemical agents.

And so a great industry today, through a combination of the marvels of electricity, chemistry, and man, has arisen out of an experiment an obscure alchemist in Hamburg in 1669 had called a failure.

Highlights of the Board of Directors' Meeting

(Held January 27, 1956)

Communications from the President

The President asked for suggestions for nominees for the Perkin Medal Award. He reported on his activities with regard to organizing an International Symposium on Passivity and advised that no definite progress has been made due to the fact that both the Faraday Society and DBG feel they cannot schedule such a session in the near future. This matter will be considered further at a later date.

The President brought up the matter of a comparative budget of the Optical Society which publishes a monthly journal on a total budget of \$47,000 a year, which is considerably less than The Electrochemical Society spends. Of the \$47,000 total, approximately \$36,000 is for printing and mailing of the journal. This is accomplished by making use of joint facilities within the American Institute of Physics. The President recommended that our Publication Committee investigate the possibility of The Electrochemical Society entering into such a joint venture.

The President read the Report of the Tellers of Election, and on motion of Dr. F. A. Lowenheim the Board approved the Report, thereby declaring Hans Thurnauer as President-Elect and W. C. Gardiner as newly elected Third Vice-President, to take office at the conclusion of the San Francisco Meeting.

Communications from the Treasurer

The Treasurer advised that income for the fiscal year 1955 amounted to \$88,690; that expenses totaled \$83,297, leaving an excess of income over expenses of \$5,393.

The Treasurer also reported on the financial status of the various funds of the Society, and on motion of Dr. Lowenheim it was voted that such a special report be made to the Board once a year. It was also decided that a report be made each year on the entire status of the monograph series. On motion of Dr. Sherlock Swann it was voted that the Treasurer's report be approved.

Dr. Gilbertson voiced his thanks to Robert Shannon for his help in accumulating data for his report.

Communications from the Secretary

The budget for the year 1956 was presented by the Secretary.

The Secretary recommended that the Society change its fiscal year from the period January 1 to December 31 to the period April 1 to March 31. This recommendation was concurred in by the Finance Committee and our auditor. This will avoid changing the fiscal year in the middle of our high income period and will make budgeting

and following of the financial affairs of the Society considerably easier. The Secretary proposed that he submit a budget at the San Francisco Board Meeting which would cover the 15-month period January 1, 1956-March 31, 1957, so that after including one 15-month fiscal period, the change would then be effected making the official fiscal year April 1-March 31. On motion of Dr. Lowenheim it was voted that the Secretary be instructed to

BUDGET FOR 1956

	Income		
	1955 Budgeted	1955 Actual	1956 Budgeted
Income from Dues.....	\$30,000	\$30,740	\$32,600
Sustaining Memberships.....	10,000	14,950	12,000
Reprints.....	3,000	4,000	4,000
Nonmember Journal Subscriptions.....	22,000	15,530	22,000
Office Sale of Journal & Back Transactions.....	600	1,180	1,000
Conventions.....		6,120	5,000
Advertising.....	16,500	14,500	14,000
Bound Volume.....			2,000
Income for General Reserve:			
Nonmember Journal Subscriptions.....			4,350
Nonmember Convention Registration.....		420	1,200
Monograph Program.....		1,250	1,250
	\$82,100	\$88,690	\$99,400
	Expenditures		
Printing & Mailing Journal.....	\$31,000	\$30,880	\$31,000
Reprints.....	2,500	2,080	2,500
Publication Committee.....	250	350	350
Advertising Commission.....	5,200	5,200	5,200
ABC Rating.....	1,000	102	
Salaries, Social Security, & Insurance.....	35,500	35,630	37,400
Rent.....	2,400	2,400	3,600
Postage, Supplies, Misc.....	6,200	5,580	6,000
Auditor.....	175	175	175
Local Sections & Divisions.....	1,000	800	1,000
Young Author's Prize.....	100	100	100
Office Equipment.....			585
Convention Expenses Less all Salary Charges:			
Program Booklet.....			1,380
Travel of N. Y. Personnel.....			1,500
Materials & Supplies.....			320
Postage & Express.....			490
Bound Volume.....			2,000
	\$85,325	\$83,297	\$93,600

Excess Income Over Expenditures to Reserves..... \$5,800

submit a 15-month budget at the San Francisco Meeting.

After considerable discussion of various other items in the budget, on motion of Dr. Lowenheim it was voted that the budget, as presented, be approved.

At this point in the meeting, the report of the Survey Committee was presented by Drs. R. M. Hunter and R. A. Schaefer. Many of the points covered in the Survey Committee report could not be discussed at this Board meeting; others called for some action immediately. On motion of Dr. Ernest Yeager it was voted that The Electrochemical Society is officially interested in the possibility of arranging for office facilities in the proposed new Engineering Societies Building. A recommendation regarding an Investment Advisory Panel was, at this stage in the meeting, referred to the Ways and Means Committee for recommendations. On motion of Mr. N. C. Cahoon it was voted that the Board express sincere appreciation for the time and effort devoted by the Survey Committee to its work. On motion of Dr. C. A. Snavelly, it was voted that the committee be discharged and that the report be referred to the Ways and Means Committee for further study and implementation. (No attempt has been made in the Highlights of this meeting to cover all the recommendations made by the Survey Committee. Only those points are alluded to in which specific action was taken at this Board meeting.)

The Secretary reported on the advertising situation; some companies have withdrawn their advertising due to the fact that it has brought no response. He also reported we had resigned from ABC and have discontinued the reader's service card.

The Electrodeposition Division recommended authority to expend up to \$500 for payment of expenses of Dr. Helmut Fischer for attendance at the Cleveland Meeting. On motion of Dr. Snavelly, it was voted to approve this recommendation.

The Corrosion and Theoretical Divisions presented their request for an appropriation from the Corrosion Handbook Fund to cover the expenses of Dr. Karl Bonhoeffer while in San Francisco. On motion of Dr. Yeager it was voted that these Divisions be authorized to spend up to \$150 to pay Dr. Bonhoeffer's expenses while resident at the San Francisco Meeting.

The problem of the India Section

(precipitated by decline in currency rates) was discussed, and President Uhlig turned over to the Secretary a check for \$115 from The Asia Foundation. This grant was made to subsidize each India member to the extent of \$5.

The Secretary brought up the matter of the necessity for moving the national office to a more suitable location. After considerable discussion, the Secretary requested authority to consummate such a move this spring. However, he expressed a desire to have a committee of New York members confer with him on this move. On motion of Dr. Swann it was voted that such a committee be appointed to work with the Secretary.

The Corrosion Division Bylaws were approved as presented to the Board (See page 98C of this issue).

The Secretary reported that, since the last meeting, our contract with John Wiley & Sons, Inc., for the monograph series has been investigated. This contract calls for this company to be our exclusive publisher.

The Secretary presented the names of F. C. Benner, Chairman; L. B. Rogers, Vice-Chairman; Charles Levy, Secretary-Treasurer; and H. Bandes and C. W. Jerome, Representatives on the Council of Local Sections, as officers for the new Boston Section. On motion of Dr. Swann it was voted that the Boston Section be officially approved.

The Secretary announced that considerable interest is manifest in forming local sections in Houston and Los Angeles, and possibly Indianapolis.

The Secretary brought up the matter of reprinting "Vacuum Metallurgy," and on motion of Mr. C. W. Jerome it was voted that we print 500 additional copies of this monograph.

Future Meetings

The Secretary presented the report of the Pittsburgh Meeting, recently received from Dr. J. P. Fugassi. This is one of the most complete and informative reports ever received.

Dr. Fielding Ogburn, General Chairman of the forthcoming Washington Meeting, reported that they are planning to hold an evening session on Wednesday, leaving Wednesday afternoon open. This met with the Board's informal approval.

Report of the Council of Local Sections

The matter of transportation to the San Francisco Meeting was discussed.

Members who are interested in either chartered air or rail transportation should contact the national office.

Reports of Committees

Ways and Means Committee

The Ways and Means Committee reported that they are planning to bring up at the next meeting changes in our Bylaws which would provide for the designation of Patron for those Sustaining Members paying \$1000 a year or more. They will also propose another change which would eliminate the 50-mile radius rule for local sections. Formal action on these Bylaw changes will be taken at the San Francisco Board meeting.

Membership Committee

The report of the Membership Committee was read by the Secretary.

Palladium Medal Committee

The President asked for the approval of the appointment of the following committee for 1957: H. A. Laitinen, T. P. May, E. B. Yeager, N. Hackerman, and J. P. Fugassi. On motion of Dr. Swann it was voted that these appointments be approved.

Finance Committee

The Finance Committee recommended that the Becket Award funds be invested 50% in Union Carbide & Carbon common stock and 50% in U. S. Treasury Bonds. After considerable discussion, on motion of Dr. Campbell it was voted that this matter be referred to the Investment Advisory Panel, with the provision that, if they are not able to make recommendations for investment within six weeks, the Treasurer is then authorized to accept the recommendation of the Finance Committee.

The Finance Committee recommended that the two reserve funds, at present known as the Publication Reserve and the General Reserve, be combined into one Society Reserve Fund since both have the same objectives. On motion of Dr. Swann it was voted that these two funds be combined.

The Finance Committee recommended that the reserve funds be invested in Treasury Bonds, and on motion of Dr. Campbell it was voted that this matter be referred to the Investment Advisory Panel with the provision that, if they do not make recommendations within six weeks, the

money be invested in U. S. Treasury Bonds as recommended by the Finance Committee. At this point, the Board

recommended that the President take immediate action to appoint an Investment Advisory Panel.

The meeting was adjourned at 4:45 P.M.

HENRY B. LINFORD, *Secretary*

Thurnauer and Gardiner to take Office at San Francisco



HANS THURNAUER

As a result of the recent annual election, in which the voting is by mail ballot, Hans Thurnauer has been elected



WILLIAM C. GARDINER

the new President of the Society, and William C. Gardiner, Third Vice-President. The new officers will take

office at 8:00 A.M. on Thursday, May 3, 1956, at San Francisco.

Mr. Thurnauer, Head of the Inorganic Section of the Central Research Laboratory, Minnesota Mining and Manufacturing Co., St. Paul, Minn., replaces Herbert H. Uhlig, professor of metallurgy in charge of the Corrosion Laboratory at Massachusetts Institute of Technology, Cambridge, Mass. Dr. Uhlig, as Past President, will continue as a member of the Board of Directors.

William C. Gardiner, Associate Director of Electrochemical Engineering in the Research and Development Division of Olin Mathieson Chemical Corp., Niagara Falls, N. Y., will start his first term as Society Vice-President and will serve with the two previously elected Vice-Presidents, Norman Hackerman and Sherlock Swann, Jr.

Lyle I. Gilbertson begins the second year of his three-year term as Treasurer.

Gordon Research Conferences, July 1956

The 1956 Gordon Research Conference on Corrosion will be held from July 16 through July 20 at Colby Junior College, New London, N. H. The Conference on Chemistry and Physics of Metals will be held from July 23 through July 27 at the New Hampton School, New Hampton, N. H.

The Gordon Research Conferences, sponsored by the American Association for the Advancement of Science, were established to stimulate research in universities, research foundations, and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and free discussion groups. Sufficient time is available to stimulate informal discussions among the members of a Conference. Meetings are held in the morning and in the evening, Monday through Friday, with the exception of Friday evening. Afternoons are available for recreation, reading, or participation in discussion groups as the individual desires.

This type of meeting is a valuable

means of disseminating information and ideas which otherwise would not be realized through the normal channels of publication and scientific meetings. In addition, scientists in related fields become acquainted and valuable associations are formed which result in collaboration and cooperative effort between different laboratories.

It is hoped that each Conference will extend the frontiers of science by fostering a free and informal exchange of ideas between persons actively interested in the subjects under discussion. The purpose of the program is not to review the known fields of chemistry, but primarily to bring experts up to date as to the latest developments, analyze the significance of these developments, and to provoke suggestions as to underlying theories and profitable methods of approach for making new progress. In order to protect individual rights and to promote discussion, it is an established rule of each Conference that all information presented is not to be used without

specific authorization of the individual making the contribution, whether in formal presentation or in discussion. No publications are prepared as emanating from the Conferences.

The first meeting of each Conference is held Monday morning at 9:00 A.M., Eastern Daylight Saving Time. The morning sessions, through Friday, are scheduled from 9:00 A.M. to 12:00 Noon. The second session of each day is held in the evening from 7:30 to 10:00 P.M., Monday through Thursday. There are no Friday evening meetings.

Accommodations are available for a limited number of women to attend each Conference, also for wives who wish to accompany their husbands. All such requests should be made at the time of the request for attendance because these limited accommodations will be assigned in the order that specific requests are received. Children 12 years of age and older can be accommodated. Dogs or other animals will not be permitted in the dormitories.

Individuals interested in attending the Conferences are requested to send their applications to the Director. Each applicant must state the institution or company with which he is connected and the type of work in which he is most interested. Attendance at each Conference is limited to 100.

Requests for attendance at the Conferences, or for any additional information should be addressed to W. George Parks, Director, Dept. of Chemistry, University of Rhode Island, Kingston, R. I. After June 11, mail should be addressed to Colby Junior College, New London, N. H.

Shown below are the programs for the 1956 Conference on Corrosion and the Conference on Chemistry and Physics of Metals.

Corrosion

J. J. Harwood, *Chairman*

W. D. Robertson, *Vice-Chairman*

July 16

Recent Advances in Electrochemistry

N. Hackerman, *Chairman*

R. Piontelli—Electrochemistry of Metals.

D. C. Grahame and I. R. Miller—The Adsorption of Polyelectrolytes on Mercury Surface.

A. J. Kolk—Recent Developments and Current Research in Fused Salt Electrolysis.

Panel Session—Implications of Progress in Electrochemistry to Corrosion.

July 17

New Researches in Passivity

M. Cohen, *Chairman*

R. Speiser—Some Aspects of Passivation.

H. H. Uhlig—Passive Films on Iron.

M. Cohen—Passivity of Iron.

Panel Session—Mechanism of Passivity.

July 18

Nucleation of Localized Corrosion

J. Petrocelli, *Chairman*

P. M. Aziz—The Probability Nature of Pitting Corrosion.

W. D. Robertson—Structure Dependent Nucleation of Chemical Reactions at Metal Surfaces.

M. A. Streicher—Nucleation of Corrosion in Stainless Steel.

Panel Session—Nucleation of Corrosion Reactions.

July 19

Kinetics of Corrosion Reactions

W. D. Robertson, *Chairman*

A. J. deBéthune—Kinetics of Heterogeneous Reactions.

A. C. Makrides—Some Studies of the Kinetics of Corrosion Reactions.

L. Epstein—Corrosion by Liquid Metals.

W. D. Manly—The Phenomena of Liquid Metal Corrosion.

July 20

Fundamentals of Protective Coatings—the "Wash Primer" System

E. R. Allen, *Chairman*

M. Bloom—The Mechanism of Protective Film Formation.

F. Eirich and R. Ullman—Polymer Resins and Their Metal Complexes in Adsorption and Adhesion.

Chemistry and Physics of Metals

Bruce Chalmers, *Chairman*

B. L. Averbach, *Vice-Chairman*

June 23-27

E. S. Machlin and A. S. Norwick—Lattice Vacancies in Crystals.

E. A. Gulbransen and A. U. Seybolt—Solid Gas Equilibria.

G. C. Kuczynski and B. E. Warren—Order-disorder.

C. Wagner and L. S. Darken—Liquid Alloy Equilibria.

O. K. Rice and A. Skapski—Theory of Liquids.

W. D. Robertson and R. B. Gordon—Structure and Properties.

R. A. Oriani and O. J. Kleppa—Thermodynamics of Solutions.

J. O'M. Bockris and R. Schuhmann, Jr.—Slag-Metal Equilibria.

A. D. Le Claire—Subject to be announced.

DIVISION NEWS

Electronics Division

The Committee on Bylaws (A. P. Thompson, H. R. Harner, and J. R. Musgrave) recommends the following revisions. These revisions will be voted on at the Annual Meeting of the Division during the San Francisco convention and will take effect at the spring 1957 convention.

Article III, Section 2

Replace with:

"The terms of office shall be two

years. The Secretary-Treasurer may serve successive terms. Other officers shall be eligible for re-election but shall not serve two successive terms."

(Note: Previously the term of office was one year; the change is recommended to be in line with the other Divisions and to insure continuity of effort. The re-election provision for the Secretary-Treasurer is made to retain the original intent.)

J. R. MUSGRAVE

The Nominating Committee (A. L. Smith, Chairman, H. R. Schoenfeldt, and J. F. Hazel) has selected the following nominees for officers during the 1956-1957 term:

Chairman—Arthur E. Middleton, P. R. Mallory & Co., Inc., Indianapolis 6, Ind.

Vice-Chairman (Luminescence)—Luke Thorington, Westinghouse Electric Corp., Bloomfield, N. J.

Vice-Chairman (General Electronics)—Lyle W. Evans, Sylvania Electric Products Inc., Seneca Falls, N. Y.

Vice-Chairman (Semiconductors)—Michael F. Lamorte, Westinghouse Electric Corp., Pittsburgh, Pa.

The term of office of Secretary-Treasurer has two more years to run. This office is now filled by M. F. Quaely, Westinghouse Electric Corp., Bloomfield, N. J.

Each nominee has given assurance of his willingness to serve if elected.

The Bylaws of the Division provide that additional nominations may be made by petition signed by five members of the Division. Such petitions must be in the hands of the Nominating Committee before the election, and the nominees must have given assurance of their willingness to serve if elected.

The election will be held at the business meeting of the Electronics Division during the Spring Meeting of the Society in San Francisco, April 29-May 3, 1956.

M. F. QUAELEY,

Secretary-Treasurer

Electrothermics and Metallurgy Division San Francisco Meeting Symposia

The Electric Arc in Inert Atmospheres and Vacuum

The Electrothermics and Metallurgy Division of the Society has planned a comprehensive symposium on electric

(Continued on page 98C)

Revised Bylaws of the Corrosion Division

(With Revisions Adopted at the Business Meeting, October 1955, and As Approved at the Board of Directors' Meeting, January 27, 1956)

Article I

NAME

(1) This organization shall be known as the Corrosion Division of The Electrochemical Society, Incorporated.

Article II

MEMBERSHIP

(1) The active membership of the Corrosion Division shall be those members of The Electrochemical Society who register their desire to be members of the Corrosion Division with the Secretary of The Electrochemical Society or with the Secretary of the Division.

Article III

MEETINGS

(1) The Corrosion Division shall hold at least one meeting annually, presided over by the Chairman of the Division. In his absence, the Vice-Chairman shall preside, or in the absence of the Vice-Chairman, the Secretary-Treasurer. In the absence of these officers, the Chairman shall appoint a presiding officer from the list of members.

The annual meeting shall be held at the Fall convention of The Electrochemical Society and the Division's activities shall be concentrated at this meeting, including the presentation of papers. Sessions or Symposia may be arranged for the Spring conventions of the Society if in cooperation with, or not in conflict with, other Division programs.

(2) Special business meetings can be called at any time, at the discretion of the Chairman or upon written request of ten members addressed to the Chairman.

Article IV

OFFICERS

(1) The officers of the Corrosion Division shall be a Chairman, a Vice-Chairman, and a Secretary-Treasurer.

(2) The executive committee of the Corrosion Division shall consist of five members, the three officers and two members of the Division appointed by the Chairman.

Article V

ELECTIONS

(1) The terms of office shall be one year. Officers shall be eligible for reelection.

(2) The officers shall be elected by a vote of the membership at the annual meeting of the Division, and shall take office immediately after the adjournment of the meeting.

(3) Any vacancy occurring during the year shall be filled as described below. In the event that the office of Chairman becomes vacant, the Vice-Chairman shall automatically become Chairman until the next election. In the event that a vacancy occurs in either the office of Vice-Chairman or Secretary-Treasurer, the Chairman shall appoint to that office a member who shall serve until the next election.

Article VI

NOMINATIONS

(1) The Chairman of the Corrosion

Division shall appoint, prior to the annual business meeting, a nominating committee of three members, which committee shall make nominations for offices under the rules listed below.

(2) Each nominee shall be notified in advance of the responsibility of the office, and the committee shall receive the nominee's assurance of willingness to serve.

(3) To insure greater continuity in the activities of the Division, the candidate for Secretary-Treasurer should be nominated on the basis that he be able to serve at least two years.

(4) Additional nominations may be made from the floor by active members of the Corrosion Division.

Article VII

ADMINISTRATION OF HANDBOOK FUNDS

(1) Royalties accruing from the sale of the "Corrosion Handbook" shall be administered, subject to approval by the Board of Directors of The Electrochemical Society, by a Committee comprised of the following:

1. Chairman of the Division.
2. A member of the Board of Directors, to be appointed by the President of the Society.
3. The Editor of the Handbook.
4. A member of the Editorial Board of the Handbook, to be appointed by the Editor.

Article VIII

DUTIES OF OFFICERS

(1) The Chairman shall have the following duties:

- (a) To preside at all meetings of the Corrosion Division.
- (b) To appoint the nominating committee of three as provided in Article VI, item 1.
- (c) To nominate two members of the Corrosion Division, one of whom shall be appointed by the President of The Electrochemical Society to represent the Corrosion Division on the Membership Committee.
- (d) To represent the Division on the Board of Directors of the Society, or to appoint a proxy if he is unable to be present at a meeting.
- (e) To appoint two members of the Corrosion Division to the Executive Committee as required by Article IV, item 2.
- (f) To represent the Division on a Committee charged with administration of income from the sale of the "Corrosion Handbook" as provided for in Article VII.

(2) It shall be the duty of the Vice-Chairman to perform all duties of the Chairman in the event of absence of the Chairman.

(3) It shall be the duty of the Secretary-Treasurer to keep an accurate record of all proceedings of the Corrosion Division, of all receipts and expenditures of money of the Corrosion Division, and to present a report to the members at the annual business meeting of the Division. A copy of this report shall be filed with the Board of Directors of the Society.

(4) The governing body of the Corrosion Division shall be the Executive

Committee, and the duties of this Committee shall be:

- (a) To determine topics for Symposia that may be sponsored by the Division, and to aid in the solicitation of papers to be presented at the annual meeting.
- (b) To determine the policies of the Division, to recommend changes of policy or amendments of these Bylaws to the Division, and to bring before the Board of Directors of the Society such recommendations as may be proper for Board acceptance.
- (c) To have jurisdiction over such special publications as the Corrosion Division may sponsor, subject to such approvals as are required by the Constitution and Bylaws of The Electrochemical Society.

Article IX

AMENDMENTS

(1) These Bylaws, or any part of them, may be amended by a two-thirds majority vote of those members attending the annual business meeting, provided a quorum is present and provided notification of the proposed changes and of the balloting was given preceding the meeting. They may also be amended by a majority vote solicited by mail from the membership by the Secretary-Treasurer, at the suggestion of the Executive Committee, or upon a request signed by fifteen members.

Article X

QUORUM

(1) Twelve members of the Corrosion Division shall constitute a quorum at meetings, the Chairman voting only in case of a tie.

(2) A majority vote shall be decisive.

Article XI

FISCAL YEAR

(1) The fiscal year of the Corrosion Division shall start immediately after the election of officers.

(Continued from page 97C)

are at its Spring Meeting to be held at the Hotel Mark Hopkins in San Francisco, April 29 to May 3, 1956. This Division, in cooperation with the Society, has made a special effort to make the meeting in San Francisco attractive to people from the East and West. As an added attraction to the technical program, the Society has made arrangements for several activities of a lighter nature for the enjoyment of members, guests, and ladies.

In general the technical program has been designed to treat the area of arc technology concerned with the theory, characteristics, and applications of high current arcs, the anode, cathode, and plasma of which are contained in a gas envelope under pressure or vacuum. Although the subject matter was originally limited to arcs in inert atmospheres and vacuum, it was considered desirable

to widen its scope to include gases which produce reactions in one or more regions of the arc.

The following preview of the papers outlines the subjects covered by the two-day symposium on arcs:

1. A film presentation of the mechanisms of metal transfer in consumable-electrode arcs.

2. A paper describing the mechanism in high intensity arcs whereby electrical input energy is transferred to the electrode material.

3. A study of the rates of burn-off of anode and cathode at various subatmospheric pressures with particular application to titanium and zirconium arc melting furnaces.

4. The results of an investigation of the effect of magnetic fields on the behavior of the arc and molten pool in the consumable-electrode arc melting process.

5. A paper describing studies of the thermal environment of material vaporized by the high intensity arc with special emphasis on conditions prevailing in the anode tail flame.

6. The study of arc characteristics as affected by different electrode materials in argon and reduced pressure including a high-speed film presentation.

7. A study of the characteristics and thermal dissipation properties of high current arcs in the five rare gases.

8. A paper on the high intensity arc in process chemistry which presents interesting applications in chemical and metallurgical processes.

9. A study of the effect of variables on the melting rate of metals, such as kind of metal, crucible to electrode size ratio, power input, etc., in the consumable-electrode arc furnace.

10. A discussion of the pressure relationship in the regions above and within the vacuum arc as applied to arc melting furnaces.

11. A paper and film presentation describing the vacuum remelting of superalloys and steels by the consumable-electrode process in terms of a comparison of the properties, gas contents, and cleanliness of air-melted and vacuum remelted materials.

12. An experimental study of a three-phase a-c consumable-electrode arc furnace and its economic and practical advantages.

13. A paper describing the construction and operation of a unique general purpose laboratory and pilot-plant arc furnace for melting in protective atmospheres and vacuum.

14. A paper treating economic and

reaction considerations of electrode requirements of the high intensity arc for metallurgical applications.

15. A paper discussing electrode control systems for inert atmosphere and vacuum arc furnaces in terms of operating characteristics and relative merits of the various regulator types.

We believe the above subject matter should arouse considerable interest because of the expanding applications of arc technology in the processing of modern metals.

WILLIAM E. KUHN,
Program Chairman

Marginal Ores and Their Relation to the National Economy

The rapid depletion of high grade ore deposits has resulted in a renewed emphasis on the low grade deposits often classed as "marginal." Improved technology for recovering valuable ore constituents and the new emphasis on minor metals make this symposium of increasing importance.

Stephen M. Shelton, Regional Director, Region I, U. S. Bureau of Mines, Albany, Ore., will be the keynoter for the meeting. In addition to Bureau activities, Mr. Shelton is well known for his role in the production of zirconium and the development of ore reserves and metallurgical processes in the Northwest.

The eight papers to be discussed at the Society Meeting in San Francisco include subjects ranging from power resources for the development of electrolytic plants in Alaska to the separation of thorium and rare earths from ores and their ultimate reduction to metal.

The symposium chairman will be A. H. Roberson, Chief, Branch of Process Metallurgy, U. S. Bureau of Mines, Albany, Ore.

A. H. ROBERSON

Atomic Reactor Fuel Processing Metallurgy

A half-day session on the pyrometallurgical processing of atomic reactor fuels will be part of the technical program for Wednesday morning, May 2, during the annual Spring Meeting in San Francisco.

The Society has been fortunate in obtaining the results of outstanding work by prominent AEC-sponsored scientists on the critical subject of reprocessing reactor fuels. This is the first session on this subject to be presented before a regular technical society.

The subject matter is of critical interest to anyone who may be concerned with the chemistry or metallurgy of reactor fuel components, and particularly with the separation of the unused uranium or plutonium fuel material from fission products and other parts of the fuel structure.

Several techniques will be presented.

1956 Extended Abstracts

The Electronics Division will again publish an "Enlarged Abstracts" booklet for the Spring 1956 convention of the Society at San Francisco. The booklet will have 1000-word abstracts of the papers to be presented before the Electronics Division in its symposium on

Luminescence
Semiconductors

The abstracts will contain pertinent information and experimental data given in the papers, and will provide these details before publication, thus aiding workers in the field. The abstracts will be "printed but not published."

The abstract booklets should be available by about April 12; the price will be \$2.00. Orders should be sent to:

Martin F. Quaeley
Research Dept., Lamp Div.
Westinghouse Electric Corp.
Bloomfield, N. J.

The Theoretical Electrochemistry Division is publishing an extended abstracts booklet of the papers to be presented at the sessions of the Theoretical Division at the Spring 1956 meeting of the Society in San Francisco. The booklet will also contain abstracts of the papers to be presented at the Symposium on "Adsorption Phenomena at Electrode Surfaces" sponsored jointly by the Theoretical Electrochemistry and Corrosion Divisions.

The extended abstract booklets can be obtained after April 16 at \$2.00 each from:

Ernest Yeager
Dept. of Chemistry
Western Reserve University
Cleveland 6, Ohio

and will be available at the registration desk at the San Francisco Meeting.

including distillation, magnesium extraction, salt extraction, electrorefining, and liquid metal extraction.

A. U. SEYBOLT

Rare Earth Symposium

A symposium on the production, physical properties, and chemistry of the rare earths will be held as part of The Electrochemical Society program at San Francisco. The program will include treatment of ores, production of metal, flame spectrometry, and the formation of lanthanum compounds.

Recent expanding interest in rare earths should promote stimulating discussions.

A. U. SEYBOLT

SECTION NEWS

Boston Section

The first meeting of the Boston Section was held on February 23, 1956 at the M.I.T. Faculty Club. A panel of speakers from Sylvania Electric Products Inc. presented a discussion of "Electroluminescence and the Panelescent Lamp." Speakers included Drs. E. F. Lowry, R. M. Rulon, J. F. Waymouth, and Mr. R. G. Slauer.

Three outstanding characteristics which make the panelescent lamp a particularly intriguing lighting development are:

1. It is a true "area" source limited in size and shape only by practical processing considerations. Since incandescent lamps are fundamentally point sources, and arc discharge lamps line sources, the panelescent lamp as an area source bridges a previous gap in the solution of structural lighting problems.
2. The lighting produced is extremely uniform, variations in brightness being almost imperceptible.
3. The lamp is cool to the touch, partially because it was introduced as a low energy source but also because its heat dissipation is spread uniformly over the entire surface so that no hot spots are produced.

As originally introduced the lamp consisted of a sheet of glass which had been treated to make one surface electrically conducting. On this surface was applied a phosphor-dielectric coating backed by a layer of evaporated aluminum.

Development of the panelescent lamp has been rapid—so rapid in fact as to result in an improved lamp of a rad-

ically different construction, which, while preserving the three important characteristics outlined above, gives such definite advantages over the earlier lamp as added physical strength, excellent maintained light output, and longer life. The new approach features layers of ceramic materials fired on to a metal plate. Since most of its weight and volume are concentrated in the metal panel, the ceramic panelescent lamp had been described as a panel of glowing metal. Unlighted it looks very much like the porcelain enamel finishes commonly found today in household appliances. Metal lamps permit a somewhat broader approach to specific applications than did the glass lamps, since holes, notches, and slots are readily formed. In addition, a wide variety of lamp shapes can be obtained. For a given shape, once tooling is available for the initial piece, repetitive parts may be produced easily making use of the relatively low cost methods of mass production.

For the present, ceramic panelescent lamps will be commercially available only for 120-v operation. Lamps for use at higher voltages have been made but complete data are not yet accumulated. These data will be published as soon as they become available. The 120-v lamps in the sizes now commercially available will draw a current of approximately 0.06 ma/in.². A clock face 3 in. in diameter would consume less than $\frac{1}{2}$ w and could be operated 24 hr a day for an entire year at a cost of about a nickel.

On 120-v 60-cycle circuits the lamps have an initial brightness of from 0.1 to 0.2 ft-L. This brightness range directs their use to applications for the dark-adapted eye. At an arm's length the panels will appear extremely uniform to the eye. By increasing the frequency of the applied voltage to the order of 400 cycles, an increase of approximately three times the 60-cycle brightness may be obtained although this depends to some extent upon the individual lamp color. Lamps designed for use at higher voltages will give materially higher brightnesses.

As mentioned above, the 120-v lamp makes an excellent source for use in cases involving the dark-adapted eye. One obvious application is a luminous clock face. Numbers and time hands silhouetted against a face are clearly visible in a darkened room at reasonable distances. Such a clock also supplies sufficient light to identify shadows

and shapes so that some "night lighting" effect is provided.

Panelescent clock faces are available commercially today in certain models of clock radios. Other potential applications include instrument panels, meter dials, signs, illuminated house numbers, and glowing plates for decorative use in the home.

The unique features of mechanical stability and durability, slow decay rather than sudden failure, and adaptability to methods of mass production, combined with inspiration on the part of designers are sure to result in many novel, interesting, and practical uses.

The next meeting of the Section is tentatively scheduled for April 17 when the program topic will be "Semi-conductors."

CHARLES LEVY, *Secretary*

India Section

Messrs. Associated Battery Makers (Eastern) Ltd., 59 C, Chowringhee Rd., Calcutta-20, and the Aluminium Industries Ltd., Kundara, have become Patrons of the Section.

An emergency meeting of the Section was held on October 14, 1955 at the Indian Institute of Science, Bangalore, with Mr. P. S. Narayana presiding. Dr. T. L. Rama Char, Secretary-Treasurer, reported that while in the U.S.A. he had detailed discussions with the President and Secretary of the Society on the question of the Society allowing a rebate on Society dues to members from India, and that the President of the Society had asked him to send a note on the subject. All the members felt that this matter should again be taken up with the Society and a detailed note sent to New York by the Secretary of the Section.

The members expressed thanks to Dr. S. Krishnamurthy, who was leaving Bangalore to join the Indian Standards Institution at New Delhi, for the excellent work done by him as Secretary-Treasurer and Editor of the *Bulletin* of the India Section.

The Second Technical Meeting of the Section for 1955 was held on December 9, jointly with the Indian Institute of Metals, Bangalore Chapter, at the Indian Institute of Science, with Professor Brahm Prakash, Head of the Dept. of Metallurgy, Indian Institute of Science, presiding. Dr. N. R. Srinivasan, Dept. of Metallurgy, Indian Institute of Science, delivered a lecture on "The Beach Minerals of Travancore and Their Beneficiation."

The present methods of beneficia-

tion such as electrostatic and electromagnetic separation used in the working of beach minerals were the main subject of the talk. After tracing the geology of South Travancore and the discovery of monazite in 1909 and the other minerals later, the composition of beach sands of Travancore were described. It was mentioned that the dunes forming in the winter carry as much as 80% ilmenite, together with other valuable minerals such as monazite, sillimanite, zircon, rutile, garnet, and several minor accessory minerals. The methods of mining are relatively simple, consisting only of collecting the washings and storing them. The ore transport was in trucks or in boats. The raw sands were treated in the factory by electromagnetic and electrostatic devices which had been locally fabricated; details of working were furnished as were illustrations of the plants. Particular attention was devoted to a method known as pneumatic tabling which was highly effective. The tonnages treated and the world production of ilmenite and other minerals were cited. The enormous possibilities that exist in the working of mineral sands both for theoretical studies and for industrial ventures were outlined.

Tables, charts, and illustrations were shown, followed by an interesting discussion period.

The Third Technical Meeting of the Section for 1955 was held on December 12 at the Indian Institute of Science, with Professor K. R. Krishnaswami, Head of the Dept. of General Chemistry, Indian Institute of Science, presiding. Professor Robert D. Vold (University of Southern California, Los Angeles, Calif.), Visiting Professor, Dept. of General Chemistry, Indian Institute of Science, delivered a lecture on "Electrokinetic Properties of Carbon Dispersions."

Professor Vold stated that the work on the electrokinetic properties of carbon dispersions stabilized with sodium dodecyl sulfate was begun originally as part of a long-range program on detergency, since it was believed that the ease of dislodgment of soil particles from surfaces and the prevention of redeposition by stabilization of the resulting dispersion would be strongly dependent on the electrical charge on the particles. Results of such studies are also of great interest with respect to calculation of the repulsive forces between suspended particles which prevent their aggregation and resultant sedimentation. Before such calculations

can be made, however, it is necessary to demonstrate the validity of the method used to derive the zeta potential on the particles from the observed electrophoretic mobility. The actual charge on the particles can also be calculated from mobility data. Comparison of the charge density with adsorption data permits determination of the degree of ionization of the adsorbed sodium dodecyl sulfate.

Carbon dispersions were prepared by initial agitation of a 0.25% suspension with a Waring Blendor at 12,000 rpm, followed by addition of the requisite quantity of sodium dodecyl sulfate, followed by an additional period of agitation at 3000 rpm. After standing 8 hr, or after mild centrifugation, the dilute supernatant suspension is suitable for observation in the microelectrophoresis cell.

Mobility measurements were carried out in a flat cell observing all the precautions pointed out by Abramson and co-workers. It was shown that the values obtained were independent of concentration of carbon in the suspension, the size of the aggregates observed in the microscope, the age of the suspension, and the current flowing through the cell. The mobility increased very rapidly with the first additions of sodium dodecyl sulfate but reached a nearly constant value independent of further change in detergent concentration at 0.03%. The mobility was the same both above and below the critical micelle concentration, i.e., the concentration (0.234%) above which the bulk of the sodium dodecyl sulfate is present as colloidal aggregates instead of simple ions.

Calculations of the zeta potential were made first by the Smolouchowski equation, and subsequently by the methods of Henry, Booth, and Stigter and Mysels. These latter treatments take into account the ratio of the diameter of the particle to the thickness of the double layer as determined by the ionic strength of the solution, with the interaction of the applied electrical field with that existing around the particle itself, together with the distortion of the field resulting from the motion of the particle (relaxation effect). In the case of suspensions studied (ultimate particles 80 m μ ; observed aggregates 1 to 3 μ) the correction for double layer thickness was negligible while corrections for the applied field increased the simply calculated potential by only 5 to 10% to a value of

about 50 mv at detergent concentrations of 0.03% or higher.

Calculation of the charge on the particles reveals the interesting fact that even though the zeta potential remains nearly constant the charge continues to increase with increasing detergent concentration. Comparison of the charge density with the number of sodium dodecyl sulfate molecules adsorbed per unit area shows that only about 3% of the adsorbed molecules are ionized when the concentration in solution is 0.01%, but that, curiously, the degree of ionization of the adsorbed molecules increases as the concentration in solution increases.

The talk was followed by an interesting discussion.

The Fourth Technical Meeting of the Section for 1955 was held on December 19 at the National Institute of Sciences of India, New Delhi, with Dr. K. L. Moudgil, Deputy Director (Chemicals), Indian Standards Institution, Delhi, presiding. Mr. S. L. Chawla, Dept. of Chemical Engineering, Delhi Polytechnic, Delhi, gave a talk on "Electrochemical Corrosion in Relation to Engineering Design."

Directory of Aluminium, 1955

The papers presented at the Aluminium Centenary Celebration in September 1955 have been published by the India Section in the Directory of Aluminium. This special number consists of 65 pages and is divided into three sections: Technical, Reference, and Directory. A limited number of copies are available at a cost of Rs.10/- per copy (payable in Indian currency only) from the Editor, India Section, The Electrochemical Society, Indian Institute of Science, Bangalore 3, India.

T. L. RAMA CHAR, *Secretary-Treasurer*

New York Metropolitan Section

The Metropolitan Section meeting on January 27 was addressed by Dr. H. H. Uhlig, President of the Society. Following a short report on affairs of the Society, he delivered a talk entitled "Corrosion as an Electrochemical Process."

The electrochemical theory of corrosion had its beginning in 1801 in a publication by Wollaston, which was followed by papers by de la Rive in 1830, and by W. R. Whitney in 1903. The original theory was applied only to rusting and acid attack. Recently it has been shown that other forms of corrosion, such as stress corrosion cracking, pitting, corrosion fatigue, intergranular

corrosion, and dezincification, are also electrochemical in nature. Considerable progress has been made toward an understanding of corrosion processes. It is possible to predict that preventative measures, with few exceptions, can be used to prevent all forms of corrosion.

With the aid of an interesting set of slides, the speaker discussed the various types of corrosive attack and described the mechanisms by which they progress. He pointed out that if the anodic areas remain fixed, pitting occurs, but if they move from place to place, an over-all type of corrosion results. The different types of cells which may function in corrosion reactions were described. It was shown how polarization curves combined with corrosion potentials can be used to calculate corrosion rates in specific instances.

A lively discussion followed the talk.

K. B. McCain, *Secretary-Treasurer*

San Francisco Section

Dr. K. K. Kelley, Superintendent, Minerals Thermodynamics Experiment Station, Region II, U. S. Bureau of Mines, was the speaker at the January 25 meeting of the San Francisco Section. His topic was "Thermodynamic Data for Metallurgical Processes."

After giving a brief history of the Bureau of Mines Station at Berkeley, Dr. Kelley told how the problems investigated by his section originate. They come from other bureau stations, from other government agencies, from within the station itself, and from established industry problems. In this connection, the station would not work for one company but would undertake thermodynamic problems common to a whole industry like steel or aluminum.

Dr. Kelley explained that the main interest of the station is to get free energy, heat content, heat capacity, and entropy data for metallurgical processes at high temperatures. This permits calculation of equilibrium constants as well as the minimum energy required by particular processes.

Dr. Kelley gave a short review of the basic thermodynamic equations which are used in his work. He indicated that most of the experimental work at this station is done by calorimetry. They have five calorimeters designed to get information on entropies, heat capacities, and heats of formation of materials at various temperatures. In addition, this station makes calculations from data available in the literature.

A discussion of the precision and accuracy attainable by calorimetric tech-

niques followed. In addition, analytical difficulties were discussed. For each part of the talk, Dr. Kelley was able to draw on his past experience in order to illustrate, with a specific example, the point he wished to make.

BERNARD PORTER

NEWS ITEMS

"Vacuum Metallurgy" in Second Printing

To satisfy the demand for the papers presented at the Vacuum Metallurgy Symposium at the 1954 Fall Meeting in Boston, a second printing of the "Vacuum Metallurgy" volume has been ordered.

This volume, containing 19 reviews and original papers by experts in the field, is available in a durable paper cover for \$5.00, less the 20% discount to Society members.

American Silver Co. Cash Award Contest

A \$1000 prize contest for engineers and designers for the best new applications of thin gauge and/or high-precision tolerance stainless steel strip was announced on January 24 by Monroe Sherman, President, American Silver Co., Flushing, N. Y.

Complete information as well as entry blanks can be obtained from: Chairman, Prize Awards Committee, American Silver Co., Flushing 54, N. Y.

Thirty-one separate cash awards will be made in the contest which closes midnight, *May 30, 1956*. The Prize Awards Committee consists of editors of leading metal papers, professors of the nation's top engineering schools, and members of the technical staff of the American Silver Co. First prize is \$350.

The contest has been instituted to stimulate America's progressive engineers and designers to create new uses

for stainless steel strip that can be rolled down to hitherto unobtainable thicknesses of as low as 0.0005 in. or to any thickness with tolerances as close as plus-or-minus 0.0001 in. Widths, in both categories, range from $\frac{1}{8}$ in. to 7 in. Awards will be made on the basis of originality and practicability.

International Journal of Applied Radiation and Isotopes

A new journal with the above title is to be published quarterly by Pergamon Press, London, with an editorial office in New York. Papers will appear in English, French, German, or Russian, with abstracts in all four languages, and complete translations can be provided. The U.K., U.S., U.S.S.R., France, and Holland have representatives on the Editorial Board, with Dr. P. C. Aebersold being chief U.S. representative. Radioisotope techniques will be emphasized.

The first issue was expected to be released about March 1 and has presumably appeared. An article in this issue of interest is "A Radiochemical Technique for Determining the Specific Surface Area of Aluminum Metal Surfaces," by John E. Lewis and Robert C. Plumb, Aluminum Research Labs., New Kensington, Pa.

Science Grants

Twenty-two grants designed to point the way to improved teaching of science and mathematics in the nation's high schools and colleges were announced on January 30 by Alan T. Waterman, Director of the National Science Foundation. The grants, totaling more than a million dollars, have been awarded to colleges, universities, and professional societies for the purpose of conducting institutes led by outstanding scientists, engineers, and mathematicians for high school and college teachers in these fields. Twenty of the grants are in support of summer institutes to be held during the summer of 1956. Two of the grants are for experimental institutes to be conducted throughout the academic year 1956-57.

"Existing and potential shortages of scientists and engineers threaten our national economic and social welfare as well as the national defense," Dr. Waterman declared in announcing the grants. "It is important that private industry, state and local governments, citizens' groups, and the Federal Government unite their efforts to see that our educational system is able to provide adequate training in technical fields

Semiconductor Issue

The November 1956 issue of the *JOURNAL* will be devoted to the subject of semiconductors. The deadline for submission of papers for consideration for this issue is *May 1*.

Three copies of each manuscript should be submitted to the Managing Editor, 216 West 102nd St., New York 25, N. Y.

for highly qualified persons in sufficient numbers. The teaching of science, mathematics, and engineering not only presupposes specialized training, but advances in these fields are so rapid today that continuing effort must be made to keep our teachers abreast of recent developments. Since many teachers operate on salaries that make it impossible for them to finance refresher courses for themselves or to give up extra work during the summer for the purpose of studying in universities or research laboratories, support for these purposes is both desirable and necessary."

Dr. Waterman expressed the hope that private foundations and industrial organizations already actively supporting similar programs will find it possible to expand their efforts. The Foundation program, now in its fourth consecutive year, is an experiment designed to stimulate, through demonstration, the creation of opportunities for college and high school teachers to attend courses in science and relevant fields especially designed for teachers and conducted by leaders noted not only for competence in their fields but for skill in presentation. The Foundation maintains continuous review and appraisal of the program, and the favorable reception it has been accorded to date indicates that it is a successful experiment.

The National Science Foundation will continue the summer institutes in the summer of 1957. Proposals from colleges, universities, and professional societies for support of 1957 summer institutes should be received by the Foundation *no later than September 1, 1956*. Preliminary inquiries and final proposals should be addressed to:

Program Director for Education in the Sciences, Division of Scientific Personnel and Education, National Science Foundation, Washington 25, D. C.

On February 12 the National Science Foundation announced 164 grants totaling about \$3,240,500, awarded during the quarter ending December 31, 1955, for the support of basic research in the natural sciences, for conferences in support of science, for exchange of scientific information, and for summer institutes for refresher training of high school and college undergraduate science teachers.

The grants were made to institutions and scientists in 36 of the States, and Hawaii and Puerto Rico. The research fields included are anthropology, astronomy, chemistry, biology, earth sciences, engineering sciences, mathematical sciences, and physics.

The research grants were approved by the National Science Board upon the recommendation of Dr. Alan T. Waterman, Director of the Foundation.

Lexington Plan for Science Teachers

A plan to increase the supply of highly qualified high school science teachers by enabling them to increase their annual incomes has been devised by Arthur D. Little, Inc., a consulting research company of Cambridge, Mass., in conjunction with the Lexington (Mass.) School Committee.

Under the "Lexington Plan," ADL will find two new graduates with bachelor's degrees in chemistry, physics, biology, or mathematics who will be given three-year contracts to fill one high school science teacher's position in the Lexington High School. At the end

of the contract, they will be qualified for full-time teaching and, consequently, will not be hired on a full-time basis by ADL. If the two candidates need education courses to qualify for teaching, the Arthur D. Little Foundation will provide scholarships for such work during the first summer.

One of the pair will teach during the first semester, and the other during the second semester. Each of them will work at ADL in their respective fields for the rest of the calendar year. Since the Lexington school system will pay the two teachers for their work at the usual rate for those with such qualifications and the company will apply its customary salary scale, the total annual income will be considerably above that possible for beginning teachers. At the end of the three years, these teachers will have enough training to enable them to work every summer at ADL or some other company while teaching full time, and so they will always be able to earn a higher rate than they could by teaching alone.

Raymond Stevens, Senior Vice-President of ADL, conceived the idea and asked a committee consisting of Professor Sanborn C. Brown, of MIT, James M. Jagger, and Dr. Austin W. Fisher, Jr., both of ADL, to implement the idea. This committee worked out details with John Blackhall Smith, Superintendent of Schools in Lexington, and Professor George P. Wadsworth, of MIT, Chairman of the Lexington School Committee. It is hoped that similar arrangements can be made with other nearby school systems.

As conceived, the Lexington Plan is one attempt to help solve the critical shortage of technical and scientific manpower that leaders in both govern-

MANUSCRIPTS AND ABSTRACTS FOR FALL MEETING

Papers are now being solicited for the Fall Meeting of the Society, to be held at the Statler Hotel in Cleveland, September 30, October 1, 2, 3, and 4, 1956. Technical sessions will be scheduled on Batteries, Corrosion, Electrodeposition, Electrothermics and Metallurgy, and Theoretical Electrochemistry (joint symposium with Electrodeposition).

To be considered for this meeting, triplicate copies of abstracts (not to exceed 75 words in length) must be received at Society Headquarters, 216 West 102nd St., New York 25, N. Y., *not later than June 15, 1956*. Please indicate on abstract for which Division's symposium the paper is to be scheduled. Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

The Spring 1957 Meeting will be held in Washington D. C., May 12, 13, 14, 15, and 16, at the Statler Hotel. Sessions will be announced in a later issue.

ment and industry have underlined as the greatest single danger-point in the nation. This shortage has been traced in part directly to insufficient good science teaching in high schools with the resultant failure to interest and the possibility of discouraging many able young people from following up scientific careers. It is hoped that the Lexington Plan will develop into an effective means for helping to deal with this problem at its source.

G. E. Researcher Wins NACE Author Award

Edward L. Simons, a research associate in the Analytical Chemistry Unit, General Electric Research Lab., Schenectady, N. Y., has been selected to receive the 1955 NACE Junior Award. The award, given annually, is for the best paper published during the year in the National Association of Corrosion Engineers' monthly periodical *Corrosion* by an author under 35 years of age.

Dr. Simons' paper, "Sodium Sulfate in Gas Turbines," dealt with metallurgical problems encountered in gas turbines burning residual fuels. Coauthors of the paper were George V. Browning and H. A. Liebhafsky, also with General Electric.

Dr. Simons' technical interests include inorganic analysis, phase equilibria, and corrosion phenomena. He received his Ph.D. degree in chemistry from New York University in 1945. He worked two years on the Manhattan Project, and was an assistant professor at Rutgers University.

Chemical Industry Corrosion Topic of NACE Meeting

Control of Corrosion in the Chemical Industry is the theme of the May 9-10 meeting of the Northeast Region, National Association of Corrosion Engineers. The meeting will be held at the University of Buffalo, Buffalo, N. Y., under the joint sponsorship of the Niagara Frontier Section of NACE and the university.

Emphasis will be on the proper use of metals and alloys to prevent corrosion. The tentative program for the technical portion of the meeting has been arranged as follows:

Wednesday, May 9

Morning—"Fundamentals of Metallic Corrosion" by Milton Stern, Metals Research Lab., Electro Metallurgical Co., Niagara Falls, N. Y.;

"Iron-Base Alloys" by S. H. Kalin, Applied Research Lab., United States Steel Corp., Monroeville, Pa.

Afternoon—"Stainless Steels" by C. P. Dillon, Carbide and Carbon Chemicals Co., Union Carbide and Carbon Corp., Texas City, Texas; "Copper and Nickel-Base Alloys" by H. O. Teeple, The International Nickel Co., Inc., New York.

Thursday, May 10

Morning—"Aluminum and Magnesium Alloys" by H. P. Godard, Aluminum Labs., Ltd., Kingston, Ont.; "Metallic Coatings," by W. W. Bradley, Bell Telephone Labs., Inc.; "Lead" by Kenneth H. Roll, Lead Industries Association, New York.

Afternoon—"Titanium, Zirconium, and Tantalum" by W. E. Lusby, Jr., E. I. du Pont de Nemours & Co., Inc.; "High-Alloy Materials" by E. D. Weisert, Haynes Stellite Co., Div. of Union Carbide and Carbon Corp., Kokomo, Ind.; "Chemical Plant Problems" by M. G. Fontana, Ohio State University, Columbus.

Further information can be obtained from: Industrial Liaison Office, University of Buffalo, Buffalo, N. Y.

AIEE Technical Conference

The American Institute of Electrical Engineers Technical Conference on "New Developments in Instrumentation for Industrial Control" will be held April 26 and 27, 1956 at the Hotel Bradford, Boston, Mass. Technical Program Chairman is Robert J. Jeffries of the Schlumberger Instrument Co. General Chairman is A. Hansen, Jr., of the General Electric Co. The ASME and ISA are cooperating with the AIEE in making this Conference a success.

The Conference will consist of four sessions: I—Information Display and Recording; II—Automatic Data Handling Systems; III—Advanced Instrumentation Systems in Industry; IV—Computer-Controlled Systems for Industry.

Copies of the program can be obtained from the National Publicity Chairman, E. T. Davis, Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia 44, Pa.

Instrument Society Conference

The Instrument Society of America has announced several interesting features in connection with its 11th Annual Instrument-Automation Conference and Exhibit (International),

scheduled for New York City, September 17-21, 1956. A well-rounded program of technical sessions, clinics, and workshops for the five-day period is planned.

Continuing its policy of encouraging advancement in the instrument industry, the society this year will inaugurate a contest for pioneering in instrumentation. The contest will have a threefold purpose—to promote new ideas and inventions, to make known the needs of users, and to bring inventors and users together for advancement of instrumentation. Details of the contest, which will be limited to products not already on the market or on the market for not more than six months, will be announced at a later date.

With the eyes of the world focused on the development of America's first satellite reported under construction, the instrument group is planning to devote one of its technical sessions to this startling development in the guided missile field, and hopes to have a model of the missile present at the exhibit.

Fred J. Tabery, Exhibit Manager, has reported from his New York office, 250 W. 57th St., that already approximately two-thirds of the available exhibit space in the recently constructed New York Coliseum has been reserved for the event.

Electromet Appoints Executive Vice-President

H. K. Intemann has been appointed Executive Vice-President of the Electro Metallurgical Co., a Division of Union Carbide and Carbon Corp., it has been announced by A. L. Foscue, President of the Electro Metallurgical Co. This Division of Union Carbide produces ferroalloys which are used principally by the steel industry in the production of alloy and stainless steels.

Mr. Intemann was graduated from Stevens Institute of Technology in 1930 with the degree of Mechanical Engineer. In that same year, he started as laboratory technician in the Haloway Corp., Bloomfield, N. J., becoming Sales Manager in 1940. In 1944, he went to the Bakelite Co., a Division of Union Carbide, as Assistant General Sales Manager in the Thermoplastics Dept., moving up to the post of Vice-President and General Sales Manager in 1953.

New "Trona" Sales Agreement

Peter Colefax, President of American Potash and Chemical Corp., and Wilson Meyer, President of Wilson & George

Meyer & Co., have announced that by mutual agreement the long-standing arrangement under which the Meyer firm has represented American Potash in the sale of "Trona" agricultural potash, borax, soda ash, and salt cake in various western sales areas will not be renewed upon its expiration in mid-1956.

The expansion of American Potash & Chemical Corp. in its field of manufacturing and the added responsibilities of the Meyer Co. in its field of distribution have resulted, in recent years, in the development of divergent interests. Both parties therefore arrived at the mutually agreeable decision to sever their old relationship.

Correction

In the paper by Robert E. Fryxell and Norman H. Nachtrieb, "Effect of Stress on Metal Electrode Potentials," in the December 1952 issue of the JOURNAL, Vol. 99, No. 12, there is an error in Reference (2) on page 503. The publication cited should be *Trans. Am. Electrochem. Soc.* rather than *Trans. Faraday Soc.*

NEW MEMBERS

In February 1956 the following were approved for membership in The Electrochemical Society by the Admissions Committee:

Active Members

- PAUL E. BLACKBURN, Westinghouse Research Labs.; Mail add: 9101 Paul St., Pittsburgh 35, Pa. (Corrosion)
 WILBUR T. BOLKCOM, American Metallurgical Products, Inc., 3600 Forbes St., Pittsburgh 13, Pa. (Industrial Electrolytic)
 FREDERIC M. BOWERS, Naval Ordnance Labs.; Mail add: 11817 Indigo Rd., Silver Spring, Md. (Battery)
 RAYMOND W. BOYDSTON, Frankford Arsenal and Films Research Corp., 7800 Governor Printz Bldg., Claymont, Del. (Corrosion, Electrodeposition, Industrial Electrolytic, Theoretical Electrochemistry)

A recent action of the Board of Directors of the Society requires that, commencing January 1, 1956, all prospective members include first year's dues with their applications for membership.

Also, please note that, if sponsors sign the application form itself, processing can be expedited considerably.

LEO BREWER, Dept. of Chemistry and Chemical Engineering, University of California, Berkeley 4, Calif. (Electrothermics & Metallurgy)

DAVID G. BROWN, Gar Precision Parts, Inc.; Mail add: Parade Hill Rd., New Canaan, Conn. (Electrodeposition)

FRANCIS X. CARLIN, Research Lab., International Nickel Co., Bayonne, N. J. (Electrodeposition)

WILLIAM H. DANCY, JR., Physics Dept., Ordnance Research Lab., University of Virginia, P.O. Box 3366, University Station, Charlottesville, Va. (Electrodeposition)

CHARLES A. FIELD, National Carbon Co.; Mail add: 1819 Pleasantdale, Suite 2, Cleveland 9, Ohio (Battery, Corrosion)

R. ARTHUR GAISER, Ball Brothers Co., Muncie, Ind. (Battery)

WAYNE L. GASPER, The Maytag Co., Newton, Iowa (Electrodeposition)

MONROE B. GOLDBERG, Naval Ordnance Lab.; Mail add: 2002 Woodberry St., Hyattsville, Md. (Battery, Theoretical Electrochemistry)

JAMES E. GREEVER, General Electric Co., #7-201, Semiconductor Products, Electronics Park, Syracuse, N. Y. (Electronics)

JOHN E. HAND, Burgess Battery Co.; Mail add: 633 W. Galena Ave., Freeport, Ill. (Battery)

VIRGINIA M. HERRIGAN, National Research Corp.; Mail add: 460 Crafts St., W. Newton, Mass. (Electronics, Electrothermics & Metallurgy)

HARRY E. IEPSON, Naval Ordnance Lab.; Mail add: 1028 Quebec Terr., Apt. #1, Silver Spring, Md. (Battery)

STANLEY KASS, Westinghouse Atomic Power Div.; Mail add: 1115 Morningside Ave., Pittsburgh 6, Pa. (Corrosion)

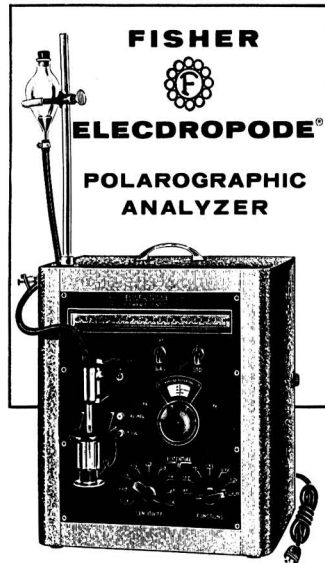
WILLIAM E. KNAPP, American Metallurgical Products Co., Inc., 3600 Forbes St., Pittsburgh 13, Pa. (Electrothermics & Metallurgy)

WALTER H. KOHL, Electronics Research Lab., Stanford University; Mail add: 12598 Valley View Dr., Los Altos, Calif. (Electronics)

PHILIP B. KRAUS, E. I. du Pont de Nemours & Co., Inc.; Mail add: RFD #1, Landenberg, Pa. (Electrothermics & Metallurgy)

HUGH L. LOGAN, National Bureau of Standards, Washington 25, D. C. (Corrosion)

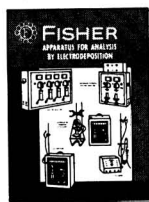
RICHARD L. MANSFIELD, National Carbon Co., Clarksburg, W. Va. (Electrothermics and Metallurgy)



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HERBERT B. REED, JR., U. S. Naval Ordnance Lab.; Mail add: 7903 Chicago Ave., Silver Spring, Md. (Battery, Electronics, Theoretical Electrochemistry)

FRANK P. ROY, Research Lab., Am. Steel & Wire Div., U. S. Steel Corp., Wire Ave., Cleveland 5, Ohio (Electrodeposition)

CHARLES A. J. SCHULTE, Vanadium Corp. of America; Mail add: 1111 91st St., Niagara Falls, N. Y. (Electrothermics & Metallurgy)

PAUL F. SCHMIDT, Philco Corp.; Mail add: 2157 Clearview Ave., Abington, Pa. (Corrosion, Electronics)

DONALD J. SCHINDEHETTE, Chrysler Engineering Div., Chrysler Corp.; Mail add: 22293 W. McNichols, Detroit 19, Mich. (Electrodeposition)

ROGER G. STEADMAN, A. B. Du Mont Labs. Inc.; Mail add: 205 Mt. Pleasant Ave., W. Paterson, N. J. (Electronics, Electro-Organic)

WILLIAM STEVEN, D. & R. Dept. Lab., The Mond Nickel Co., Ltd., Birmingham 16, England (Corrosion, Electrodeposition, Electronics, Electrothermics & Metallurgy, Theoretical Electrochemistry)

LESLIE TITUS, Kaiser Aluminum & Chemical Corp.; Mail add: 275 W. Campbell Ave., Campbell, Calif. (Electronics, Electrothermics & Metallurgy, Industrial Electrolytic)

Student Associate Member

WILLIAM F. KIRK, New York University; Mail add: 3460 Bailey Ave., New York 63, N. Y. (Electrothermics & Metallurgy)

Transfer from Associate to Active Membership

EDWARD F. FOLEY, JR., Enthone, Inc.; Mail add: 222 Augur St., Hamden, Conn. (Corrosion, Electrodeposition, Industrial Electrolytic, Theoretical Electrochemistry)

Transfer from Student Associate to Active Membership

ERIC RAU, Bettis Plant, Westinghouse Electric Corp.; Mail add: 331 Devonshire St., Pittsburgh 13, Pa. (Corrosion, Electrothermics & Metallurgy, Theoretical Electrochemistry)

Resumed Active Membership

W. C. GARDINER, Research Dept., Olin Mathieson Chemical Corp., P. O. Box 480, Niagara Falls, N. Y.

Deceased—Reported in January

D. F. BROWN, Linden, N. J.

PERSONALS

MYRON B. DIGGIN has been appointed Vice-President and Director of the Hanson-Van Winkle-Munning Co., Matawan, N. J. Mr. Diggin has been with H-VW-M for 25 years. He was Technical Director for the past nine years and was made an assistant vice-president in 1954. His work has resulted in a number of developments and patents, particularly in the depositing of cadmium, zinc, and lead, in rack coatings, anode diaphragms, and regenerative plating systems. During the past year he has worked on the specific development and use of H-VW-M electrochemical processes.

J. B. MOHLER has been engaged as a research chemist with Kaiser Aluminum & Chemical Corp., Spokane, Wash., since the first of the year. His duties are in the Finishing and Electrochemical Applications Branch of the Dept. of Metallurgical Research. Mr. Mohler holds a M.A. degree in physical chemistry from Western Reserve University. His background since 1933 includes several years as metal finishing consultant, 14 years in the sleeve bearing industry, and 7 years as research assistant for the Grasselli Chemical Lab. of E. I. du Pont de Nemours & Co.

L. J. BALASUNDARAM, of India, is now at the University of Sheffield in England for advance studies in metallurgy.

LEONARD F. YNTEMA, director of research at Fansteel Metallurgical Corp., North Chicago, Ill., has been appointed by the National Advisory Committee for Aeronautics as a member of the Subcommittee on Power Plant Materials.

JOHN G. DEAN, chemical and metallurgical consultant, Tuckahoe, N. Y., has been retained by the Climax Molybdenum Co. to advise on certain aspects of the company's recently expanded chemical program, which includes development of new and expanded applications for molybdenum compounds in catalysis, lubrication, agriculture, and pigments, as well as research into other fields where molybdenum chemicals are of potential value. In addition to acting as a consultant to

several large chemical and metal companies, Dr. Dean is associated with Columbia University. At present he is on leave from their Division of Cooperative Research to handle a strategic metal processing program.

R. M. HUNTER, Dow Chemical Co., Midland, Mich., has been elected to the Board of Directors of the Chlorine Institute, Inc., New York City, trade association of the chlorine manufacturing industry.

QUENTIN H. MCKENNA, formerly of Cleveland, Ohio, has moved to Whittier, Calif., to join the American Potash & Chemical Co. in the electrochemical division of their research facilities.

PETER ENSIO, formerly with the Quebec Iron and Titanium Corp., recently became an industrial consultant. He holds a D.Sc. degree from the Massachusetts Institute of Technology and has been active as a metallurgist both in Canada and in Europe.

CLARENCE C. ROSE

Clarence C. Rose, for many years an active member of the Cleveland Section of The Electrochemical Society, died at his home of a heart ailment on December 16, 1955.

A native Clevelander, born in 1894, Mr. Rose spent most of his life in this city, receiving his degree from the Case Institute of Technology in 1916. He was a member of Sigma Xi and Tau Beta Pi.

His career was with the Willard Storage Battery Co. which he joined in 1922 after working for shorter periods with the Dow Chemical Co. and The Damascus Oil Co. of Oklahoma. At the time of his death, he was Assistant Chief Engineer and Director of the Laboratories for Willard.

Mr. Rose was a member of The Electrochemical Society, The American Chemical Society, and The American Society for Testing Materials. He took an active part in the affairs of these groups, especially The Electrochemical Society, both on the local and the national level. His publications include several annual reviews on batteries for the TRANSACTIONS OF THE ELECTROCHEMICAL SOCIETY. In later years, he published two outstanding reviews, one on sulfation, another on battery additives for the Society's JOURNAL. He was one of the prime movers in organizing the Battery Division of the Society

and served as its Chairman for two years.

Other activities for the ECS included Society Representative on Storage Batteries for the American Standards Association, and membership on the Acheson Award Committee. He was also the author of an article on Storage Batteries for the Encyclopedia Britannica.

The forthright manner and cheerful personality of Mr. Rose won him many friends in this Society and other circles.

He is survived by his wife, Marie Mattingly Rose.

LITERATURE FROM INDUSTRY

"CORROSIONOMICS." New bimonthly publication containing useful information for the solution of corrosion problems is being distributed without charge. The Jan. 1956 issue features an article entitled "High Temperature Distillation Process Simplified with Tantalum Equipment" and has a listing of booklets and technical data bulletins that are available on request. *Fansteel Metallurgical Corp.*, Chemical Equipment Div., North Chicago, Ill.

"A REVIEW OF THE ZINC INDUSTRY IN 1955." New 13-page booklet, available without charge, summarizes the production and consumption picture of the zinc industry as it appeared to be as of Dec. 31, 1955. Comprehensive tables cover such topics as mine production, imports of slab and ore, tariff rates, slab zinc consumption, zinc uses by grades, and production of slab zinc according to grade. *The American Zinc Institute, Inc.*, 60 E. 42nd St., New York 17, N. Y.

METALLIC SOAPS. A 30-page booklet about metallic soaps is available. One of the features of the booklet is a complete history of metallic soaps and a description of the role they play in today's industry. Also given is a complete descriptive listing of Metasap metallic soaps, including physical and chemical characteristics and industrial applications. *Metasap Chemical Co.*, Dept. M., Harrison, N. J.

CERAMIC TRANSDUCERS. Comprehensive 2-color brochure covering the use of piezoelectric ceramic transducers is available. It outlines the many applications of ceramic transducers, including ultrasonic, shock and vibration, medical and underwater sound equip-

ment, in addition to presenting complete physical and electrical properties and specifications for the ceramic materials. *Gulton Mfg. Corp.*, Metuchen, N. J.

H-VW-M SELENIUM RECTIFIERS. A 2-color, 12-page technical bulletin, ER-107, describes and illustrates the H-VW-M Selenium Rectifiers for electroplating, anodizing, and related processing. Listed are construction, electrical, and control features. Also included are the specifications of standard bench, self-contained, and remote controlled types of rectifiers. *Hanson-*

Van Winkle-Munzing Co., Church St., Matawan, N. J., Att. J. S. Karinja.

"TRONA" LITHIUM HYDROXIDE. A bulletin on "Trona" lithium hydroxide has been issued providing information on potential uses, results of laboratory tests on lithium base greases and other material. In addition, it contains information on the new San Antonio lithium hydroxide plant of American Lithium Chemicals, Inc., a subsidiary of American Potash & Chemical Corp. *American Potash & Chemical Corp.*, 3030 W. 6th St., Los Angeles 54, Calif.

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"HOW TO WRITE TECHNICAL REPORTS AND STILL MAINTAIN YOUR SANITY." Booklet, originally prepared for engineers of a leading military defense laboratory and being used by several commercial research laboratories and college English departments, is now generally available at the following prices: 1-99 copies, 25¢ each; 100-500 copies, 20¢ each; over 500 copies, 15¢ each. *Technical Marketing Associates, Inc.*, Concord, Mass.

CHEMICAL SAFETY DATA SHEET, SD-2, BENZENE. Revised safety data sheet on benzene has been published. The 20-page booklet, part of a continuing series, gives properties and essential information for the safe handling and use of benzene, including material on shipping containers, storage, waste disposal, and health hazards and their control. Copies are 30¢ each. *Manufacturing Chemists' Association*, 1625 Eye St., N.W., Washington 6, D. C.

NEW PRODUCTS

FISHER-BOROLITE CRUCIBLE. "Boro-lite" zirconium boride 101 is the basis of a new Fisher crucible with superb high temperature and corrosion-resistant properties. The new tough crucible, designed to be a workhorse in metallurgical labs, has a melting point of 3900°F. Available in a 50-ml size and in a 100-ml diameter. *Fisher Scientific Co.*, 717 Fisher Bldg., Pittsburgh 19, Pa.

SUBMINIATURE SELENIUM RELAY RECTIFIER. A versatile subminiature selenium relay rectifier to energize d-c

To receive further information on any New Product or Literature from Industry listed, write directly to the company at the address given in each item.

relay coils has been developed. This new unit, Type 60-9267, is a full-wave center-tap rectifier and may be used either as a center-tap full-wave rectifier or as a half-wave and "back-wave" rectifier combination for compact relay power supply. Bulletin SR-124 available. *International Rectifier Corp.*, Product Information Dept., El Segundo, Calif.

"AIRKORE" SELENIUM RECTIFIER. A selenium TV rectifier series utilizing a new concept in surface contact while retaining the reliable "center support" construction has been announced. This new type of construction, called "Air-Kore," features a unique open-spaced six contact spring which provides greater contact area and a uniform temperature rise across the surface of the rectifier plate. *International Rectifier Corp.*, Product Information Dept., El Segundo, Calif.

YARDNEY SILCAD. A revolutionary new battery, combining the weight and size advantage of a silver-zinc couple with the long life characteristics of a nickel-cadmium couple, is available. Known as the Yardney Silcad, the battery substitutes silver for nickel in conjunction with a newly developed cadmium plate. Long battery life, high capacity, low weight, and reduced size result. *Yardney Electric Corp.*, 44 Leonard St., New York, N. Y.

REGULATED D-C POWER RECTIFIER. A regulated, 14/28 v, 200/100 amp d-c power rectifier, designed to meet Air Force specifications, is available for commercial application. Magnetic amplifier maintains desired output voltage regardless of variation in input voltage, frequency, or load. Booklet H-1 available. *Rapid Electric Co.*, 2881 Middletown Rd., Bronx 61, N. Y.

EMPLOYMENT SITUATIONS

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CHEMIST OR METALLURGIST wanted to work at the National Bureau of Standards as a Research Associate of the American Electroplaters' Society. Post-graduate work or research experience required and background in physics or physical chemistry desired.

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Reply to Mr. Fielding Ogburn, National Bureau of Standards, Washington 25, D. C.

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CHEMICAL ENGINEER, 40, B.S. degree, 14 years' experience, including materials engineering and research, electrodeposition processes, product engineering and development work involving capacitors. Reply to Box 358.

CHEMICAL ENGINEER, experience in high temperature process development, including fused salt electrolysis, electric furnaces, metals extraction, B.Ch.E. 1939, married, age 38, seeking challenging, mature position. Reply to Box 359.

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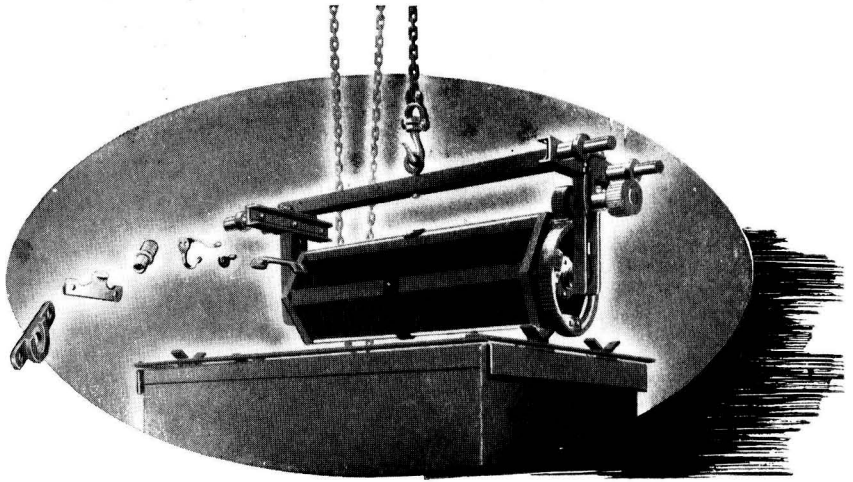
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American Machine & Foundry Co., Raleigh, N. C.
American Platinum Works, Newark, N. J. (2 memberships)
American Potash & Chemical Corp., Los Angeles, Calif.
American Potash & Chemical Corp. (Nevada), Henderson, Nev.
American Zinc, Lead and Smelting Company, St. Louis, Mo.
Auto City Plating Company Foundation, Detroit, Mich.
Bart Manufacturing Company, Bellville, N. J.
Becco Chemical Div., Food Machinery & Chemical Corp., Buffalo, N. Y.
Bell Telephone Laboratories, Inc., New York, N. Y.
Bethlehem Steel Company, Bethlehem, Pa. (2 memberships)
Burgess Battery Company, Freeport, Ill. (4 memberships)
Canadian Industries (1954) Limited, Montreal, Canada
Carborundum Company, Niagara Falls, N. Y.
Chrysler Corporation, Detroit, Mich.
Columbia-Southern Chemical Corporation, Pittsburgh, Pa.
Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C. (2 memberships)
Corning Glass Works, Corning, N. Y.
Crane Company, Chicago, Ill.
Diamond Alkali Company, Cleveland, Ohio (2 memberships)
Dow Chemical Company, Midland, Mich.
Wilbur B. Driver Company, Newark, N. J.
E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.
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Eaton Manufacturing Company, Stamping Div., Cleveland, Ohio
Electric Auto-Lite Company, Toledo, Ohio
Electric Storage Battery Company, Philadelphia, Pa.
Electro Metallurgical Company, Division of Union Carbide & Carbon Co., New York, N. Y.
The Eppley Laboratory, Newport, R. I.
Ford Motor Company, Dearborn, Mich.
General Chemical Division, Allied Chemical & Dye Corporation, New York, N. Y.
General Electric Company, Schenectady, N. Y.
General Motors Corporation, Research Laboratories Division, Detroit, Mich.
Gould-National Batteries, Inc., Depew, N. Y.
Graham, Crowley & Associates, Inc., Chicago, Ill.
Great Lakes Carbon Corporation, Niagara Falls, N. Y.
Hanson - Van Winkle - Munning Company, Matawan, N. J. (2 memberships)
Harshaw Chemical Company, Cleveland, Ohio (2 memberships)
Hooker Electrochemical Company, Niagara Falls, N. Y. (3 memberships)
Houdaille-Hershey Corporation, Detroit, Mich.
International Graphite & Electrode Div., Speer Carbon Company, St. Marys, Pa. (2 memberships)
International Nickel Company, Inc., New York, N. Y. (2 memberships)
Kaiser Aluminum & Chemical Corporation, Division of Metallurgical Research, Spokane, Wash.
Mathieson Chemical Corporation, Niagara Falls, N. Y. (4 memberships)
McGean Chemical Company, Cleveland, Ohio
Merck & Company, Inc., Rahway, N. J.
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National Carbon Division, Union Carbide and Carbon Corporation, New York, N. Y. (2 memberships)
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Niagara Alkali Company, Niagara Falls, N. Y.
Norton Company, Worcester, Mass.
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Phileo Corporation, Lansdale, Pa.
Philips Laboratories, Inc., Irvington-on-Hudson, N. Y.
Potash Company of America, Carlsbad, N. Mex.
Promat Division, Poor & Company, Waukegan, Ill.
Ray-O-Vac Company, Madison, Wis.
RCA Victor Division, Radio Corporation of America, Harrison, N. J.
Solvay Process Division, Allied Chemical & Dye Corporation, Syracuse, N. Y. (3 memberships)
Stackpole Carbon Company, St. Marys, Pa.
Standard Steel Spring Division of the Rockwell Spring and Axle Company, Coraopolis, Pa.
Stauffer Chemical Company, San Francisco, Calif.
Sylvania Electric Products Inc., Bayside, N. Y. (2 memberships)
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Tennessee Products & Chemical Corporation, Nashville, Tenn.
Udylite Corporation, Detroit, Mich. (2 memberships)
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Vanadium Corporation of America, New York, N. Y.
Victor Chemical Works, Mt. Pleasant, Tenn.
Wagner Brothers, Inc., Detroit, Mich.
Western Electric Company, Inc., Chicago, Ill.
Westinghouse Electric Corporation, E. Pittsburgh, Pa.
Wyandotte Chemicals Corporation, Wyandotte, Mich.
Yardney Electric Corporation, New York, N. Y.



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