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## Editorial



#### **Research of the Future**

EVERY research establishment has the problem of acquiring new personnel and of trying to ensure an able staff for future years. Graduate and professional schools long have had similar problems: how and when to make firm commitments to prospective students, without being over-hasty or, on the other hand, letting the prizes slip away. Right now the colleges are not immune: they are confronted with a rising tide of students, great pressure from parents and alumni, and a flood of multiple applications. Dr. E. S. Wilson, Dean of Admissions at Amherst College, gives us a glimpse of what may happen (College Board Review, Fall 1958).

From a vantage-point in the future, Dean Wilson recalls that in 1958 the Heavenly Seven (a constellation of women's colleges) announced that they would grant acceptances to a limited number of high school girls at the end of the junior year. This was expected to reduce the number of multiple applications and lead to some serenity in the high schools. Unfortunately, in the first year the number of applicants was many times more than could be considered, and the large number of rejections raised havoc with high school morale. To make matters worse, the Mundane Many (the other women's colleges) promptly started accepting the rejects as having already been screened. In fact, by 1961 the Mundane Many started accepting students at the end of the 9th grade (after all, a good student usually continues to do good work, the problems of the admissions staff are greatly eased, and, at worst, the college is protected by escape clauses in very fine print). The Heavenly Seven decided to commit themselves to acceptance of extremely able girls at the end of the 6th grade.

In the meantime, says Dr. Wilson, the men's colleges were following suit. Over the course of the years they learned, to their dismay, that one thing had been forgotten: they were getting "all brains and no brawn," which was embarrassing, and even undemocratic. A feverish search developed to select, at the age of 10, the athletes of 18. The Ivy League and the Little Three secured special funds for a research project called "Locating Talented Youth at Age 10." Ostensibly, the project was to locate intellectual talent but, since this problem had already been solved, most of the funds were used in trying to identify "qualities over and beyond the intellect," as it was phrased by one Dean.

The Mundane Many organized a committee to investigate the possibility of college acceptance at the end of the kindergarten year. The project was financed, in great secrecy, by a foundation which was very much excited by the prospect of identifying, at the age of 6, the future female scientists and engineers of the nation. By 1965 an extremely satisfactory criterion was found: an adaptation of an ancient Chinese vocational choice test. In front of the girl, several objects were placed: a flower, a bible, a doll, a false face, some silver dollars, a slide rule. Yes, you guessed the rest.

Eventually, the Heavenly Seven backed exhaustive research to detect college talent in the prenatal stage. Preliminary research turned up promising leads, especially the discovery of a new gene, which was very small and had no fixed position in the chromosome. For this reason it was called the "orbiting gene," and there was soon evidence that, indeed, it determined the student's behavior when she was launched into the college orbit.

Clearly, the Personnel Divisions should not allow themselves to be outdone by the college Board of Admission. Leaders in the Research of the Future should have exceptionally outstanding scientific teams about 30 years hence! —CVK

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#### **Batteries with Solid Ion Exchange Electrolytes**

#### I. Secondary Cells Employing Metal Electrodes

#### W. T. Grubb

Research Laboratory, General Electric Company, Schenectady, New York

#### ABSTRACT

Highly conducting ion exchange polymers can be employed as solid electrolytes in batteries. Their resistivities are intermediate between aqueous electrolytes and the usual inorganic solid electrolytes. Cells containing pairs of metal electrodes behave reversibly. Their emf's form an additive series for the examples tested and are only slightly less than those of their aqueous analogs.

In this paper the phrase ion-exchange battery is used to denote a galvanic cell in which the electrolyte is a solid (although somewhat hydrated) ionically conducting ionizing polymer of the type commonly called ion exchange resins. In these materials the self-diffusion rates and ionic conductances are simply interrelated as has been demonstrated by Coryell and Spregler (1).

Ion exchangers have been used as separating membranes in cells containing two or more electrolyte compartments such as the Daniell cell disclosed by Juda, *et al.* (2) and the concentration battery proposed by Meyer (3). They have been employed to depolarize cells by removing a reaction product (4, 5). They have been employed to supply a reacting ion to the cell reaction. For example, Robinson (6) has disclosed the use of a permanganate anion exchange resin as a cathode depolarizer in an analog of the Leclanché cell.

The present investigation has been concerned with the ion exchange polymers acting as electrolytes wherein the current is entirely conducted by the ionizing polymer itself. At the same time it maintains the physical structure of the cell. The role of the ion exchanger is analogous to that of a silver halide in the more conventional type of solid-electrolyte cells (7) except that the conductance is several orders of magnitude higher. Also, there are more possibilities for the ion-exchange battery since the mobile ion may be selected at will simply by exchanging the electrolyte into a suitable ionic state.

#### **Materials and Methods**

Ion exchange membranes.—Synthetic polymers containing strongly ionized sulfonate groups were used. A review (8) of the typical ion-exchange properties and structures may be found helpful. Particular use was made of ion-exchange membranes which consist of sheets of ion-exchange polymer very resistant to direct flow of liquids but highly permeable to ions. Two commercial membranes were employed: Amberplex C-1,<sup>1</sup> a sulfonated polystyrene resin finely comminuted and held in a matrix of an inert polymer; and Nepton CR-51,<sup>2</sup> a homogeneous sheet

<sup>1</sup> Rohm & Haas Co., Resinous Products Div., Philadelphia, Pa. <sup>2</sup> Ionics, Inc., Cambridge, Mass.

of sulfonated phenol formaldehyde polymer. These two membranes possess somewhat different electrical and mechanical properties. Hereafter they are referred to as Amberplex and Nepton membranes, respectively.

Conditioning of membranes.-The ion-exchange membranes were converted into a desired ionic form by successive equilibration in several portions of a solution of the cation in question as described by Juda, et al. (9). In all cases, the "free" electrolyte was removed by extensive washing with distilled water. In several cases the membrane was equilibrated with water in ethylene glycol, using a large excess of solution and equilibrating for 24 hr or more. The solution contained 12.0% by weight of water or a mole fraction of 0.32. The water-ethylene glycol system obeys Raoult's law (10) approximately. Solvating liquids.—Laboratory distilled ( $\rho = 500,000$ ohm-cm) water was employed as the aqueous solvate to saturate the membranes. Ethylene glycol, U.S.P. grade, was redistilled at reduced pressure under dry N<sub>2</sub> atmosphere.

Cell construction.—Two cell construction methods have been employed in this work. For high-area cells  $(A = 10 \text{ cm}^2)$  the metal foils have been backed up by  $\frac{1}{2}$ -in. plexiglas blocks, and the electrolyte has been sealed from evaporation by surrounding it with a silicone rubber gasket. In these cells, the electrolyte overlaps the electrodes to prevent any possibility of edge shorting. Low-area cells  $(A = 0.3 \text{ cm}^2)$ were constructed in trubore tubing  $(\frac{1}{2} \text{ in. ID})$ . In this case the electrode and the electrolyte do not overlap but are of the same size, being cut with the same punch and die. Data obtained on the two sizes of cells were mutually consistent.

The metals were of commercial purity, except for copper which was oxygen-free.

Electrical measurements.—Potential measurements were usually made with a Rubicon potentiometer to the nearest millivolt. Currents were obtained to about  $\frac{1}{2}$ % using a Sensitive Instrument Co. polyranger. These measurements are adequate to the purpose at hand.



Fig. 1. Schematic diagram of silver-zinc cell. Left, uncharged cell, emf 0.8-1.2 v; right, charged cell, emf 1.4-1.5 v.

#### Results

Among the possible combinations of electrode and ion-exchanger electrolyte, those in which a metal is in contact with an electrolyte containing ions of the same metal coordinated with the fixed sites on the polymer are probably the simplest. While these might be constructed as primary cells by the use of two metals and two ion-exchange membranes in appropriate ionic state, a simpler method is to form such a cell by charging a single-electrolyte cell. The process is shown diagrammatically in Fig. 1. The cell initially contains an electrolyte in the zinc state between zinc and silver foils. The charging current produces a silver ion region next to the silver electrode.

In order to prove the nature of the charging process, the cell was set up as in Fig. 1 and charged with a known current for a measured time interval. It was then disassembled, the electrolyte washed, and analyzed. The total charge input was 2.00 ma for 4.08 hr, corresponding to 32.8 mg Ag. The analysis for total silver in the membrane was 32.0 mg Ag, indicating quantitative agreement within the error of measuring the total charge.

Both phenolic (Nepton type) and polystyrene (Amberplex type) electrolytes were employed in silver-zinc cells. Measurements of cell voltage as a function of both charging and of discharging current reveal that the emf is a linear function of the current, with the line passing smoothly through the zero current axis, as seen from representative plots in



Fig. 2. EMF vs. current for Amberplex membrane cells. Numbers on curves refer to experiment numbers in Table I.



Fig. 3. EMF vs. current for Nepton membrane cells. Numbers on curves refer to experiment numbers in Table I.

Fig. 2 and 3. Table I identifies the compositions and dimensions of the various cells, and the first column refers to the appropriate curve of Fig. 2 and 3. Data were obtained at  $25^{\circ} \pm 0.05^{\circ}$ C.

In every case the cell was charged at 2.0 ma for 30 min. From the measured capacity data for the H<sup>+</sup> form of the ion exchange membranes, this amount of charge supplies the more noble metal ion to about 4% of the sites in the electrolyte (the membrane capacities per unit volume are similar for Amberplex and Nepton membranes). The data of Fig. 2 and 3 are the emf values after about 10 sec on the given load (or charge).

It might be supposed that concentration polarization is prevented by the nature of the ion exchanger electrolyte since the distribution of ions and their concentrations are held nearly constant by the immobile polymer network. However, concentration polarization actually does occur in the present cells when they are placed on heavier loads for short time intervals. This may be caused by solvate moving with the ions as hydration shells (11).

The present cells are analogous to cells with liquid junctions in conventional electrochemistry. It is likely that liquid junctions are absent in the present cells; first, because of the nature of the electrolyte which requires that the transference number is unity for cations, and second, because of the fixed sites in the network polymer, cross diffusion at the bound-

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Expt. No.	Metal pair	Type of electrolyte	Solvate	Area of cell, cm²	Thick- ness of cell, cm
1.	Ag-Zn	Amberplex	H <sub>z</sub> O	10.0	0.088
2.	Ag-Zn	Amberplex	H <sub>2</sub> O + ethylene <sup>a</sup> glycol	10.0	0.088
4.	Cu-Zn	Nepton	H <sub>2</sub> O + ethylene <sup>a</sup> glycol	10.0	0.081
5.	Ag-Zn	Nepton	H <sub>2</sub> O + ethylene <sup>α</sup> glycol	10.0	0.081
3.	Ag-Cu	Nepton	H₂O + ethylene <sup>a</sup> glycol	10.0	0.081

<sup>a</sup> Concentration = 12.0% by weight of water.

ary of the regions of different ionic form occurs in the manner of an ion exchange reaction and is therefore equal in each direction.

The lines in Fig. 2 and 3 were determined by the method of least squares. In Table II are tabulated the constants for the equations of these lines, which all are of the form, E = A - bi with E in practical volts and i in milliamperes.

The correlation coefficient (12), r, is a measure of the degree to which the least squares line represents the experimental points. It may be concluded that the experimental points are quite well represented by straight lines of constant slope, and therefore within errors of measurement the half-cells of the type metal/ion-exchange polymer, metal salt are reversible when metals such as silver, copper, or zinc are employed. Further evidence of the reversibility of the metal-ion exchanger half-cells is the additivity of potentials using the same electrolyte. From the data of experiments 3, 4, and 5 it is observed that  $A(3) + A(4) = 1.46_4$  and  $A(5) = 1.46_0$ .

The internal resistances of the cells are equal to  $b \ge 10^3$  and represent a composite of two ionic forms of the ion exchanger.

Experiments 1 and 2 illustrate the fact that solvation of the electrolyte has little effect on the emf of a typical cell but has a large effect on the internal resistance. The very slight variation of emf observed when the water activity in the ion exchanger is reduced by a factor of about 3 indicates that the activity ratio of the two ions in the electrolyte is virtually unaffected by the partial removal of the water of solvation and its replacement by ethylene glycol. This effect could be interpreted as being due to the change of dielectric constant which influences the activity of ions in ion exchangers in a manner unspecific as to the nature of the ion. The very marked effect on conductivity is probably caused by a variation in the amount of association between the fixed sites and the mobile ions. This would also be expected from variation of the dielectric constant of the solvating liquid.

A number of cells were put through charge and discharge cycles. In a typical case, a cell of the type of experiment 1, Table I, was charged for 5 hr at 1.0 ma and then placed on a fixed load resistance. The discharge current as a function of time is plotted in Fig. 4. After 5 hr, there had been recovered approximately 80% of the charge input. When cells of the type of experiment 5, Table I, were tested in a similar manner, the charge recovery was only about 40%. Little charge could be recovered from cells



Fig. 4. Discharge current vs. time for Amberplex electrolyte cell. Dimensions: d= 0.088 cm, A = 35 cm²; local resistance = 420 ohms; charge == 1 ma for 5 hr.

Table II.

which were charged and then allowed to stand for 24 hr before discharging.

Figure 1 represents an idealized situation. The boundary between ionic forms is not sharp as shown but becomes "smeared out" by cross diffusion, and this happens rather quickly in highly conducting systems. Moderate stability is produced by use of partial aqueous solvation, using solutions of water in another polar liquid (e.g., ethylene glycol). Even in this case, silver ions eventually reach the zinc electrode and deposit because of cross diffusion. Such processes destroy the cell for practical purposes.

To prevent silver ion from reaching the zinc foil a barrier layer is needed. One way of achieving this is by use of a highly selective ion exchange resin, and some progress toward this has already been made (13). A more versatile solution perhaps lies in the use of complex ions. If one ion of the cell pair forms a stable complex anion, then an anion exchange resin membrane would effectively protect the less noble metal foil. This modification of the basic cell has not been tried yet experimentally.

The present paper discussed the application of ion exchange resins as solid electrolytes in a secondary cell system employing two metal electrodes and demonstrated that these cells are electrochemically reversible. A study of several types of primary cells employing ion exchange resin solid-state electrolytes has been made and will be reported in a subsequent publication.

#### Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1959 JOURNAL.

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#### Controlled Potential Reactions of Cadmium and Silver in Alkaline Solution

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#### ABSTRACT

Data are reported on the electrochemical oxidation and reduction of both cadmium and silver in potassium hydroxide electrolyte obtained using techniques in which the overpotential was the independent and the current the dependent variable. The rate of oxidation of cadmium is maximum at overpotentials of 18.0 and approximately 40.0 mv. The rate of reduction of cadmium and the rate of oxidation of silver are both monotonically increasing functions of the overpotential.

Very few electrochemical reactions are investigated by methods which use the overpotential as the independent and the current as the dependent variable. However, the application of such methods to investigations of electrochemical reactions which produce insoluble oxide films on the electrode yields information on the kinetics of the reaction not realizable by the conventional procedures which utilize the current as the independent variable (1). Methods utilizing control of the overpotential have here been applied to the study of reactions of cadmium and silver in potassium hydroxide electrolyte with new and important results.

It is well known that the rate of most electrochemical reactions depends exponentially on the overpotential, therefore a measurement of rate as a function of overpotential is inherently a more sensitive indicator of the kinetics of the reaction than a measurement of the overvoltage as a function of the current. Furthermore, given the overpotential as an independent variable we can choose from a number of possibilities a particular reaction for investigation. If the current is the independent variable, the electrode system may seek the kinetically most favorable reaction, especially if the electrode tends toward passivity, rather than the reaction under investigation. By controlling the overpotential we can determine the influence on the reaction rate of thickening of the oxide layer with time. For example, if the rate-limiting step in the oxide growth is transport of ions through the oxide already formed on the electrode and if the driving force is a gradient in the electrostatic potential, the current density is given by

$$I = \left(\frac{\sigma\phi}{2\Omega}\right)^{1/2} t^{-1/2}$$
 [1]

If the driving force is a gradient in ion concentration, the current is given by

$$I = \left(\frac{kT}{e} \frac{.\sigma}{2\Omega}\right)^{1/2} \left(1 - \exp\left(-\frac{e\phi}{eT}\right)^{1/2} t^{-1/2} \quad [2]$$

The quantity  $\phi$  is the overpotential,  $\sigma$  the ionic conductivity, *T* the temperature, *t* the time,  $\Omega$  the volume of oxide formed per coulomb of electricity, and *k* and *e* are the Boltzmann constant and the charge on the electron, respectively.

Equations [1] and [2] indicate that, if experimental conditions are such that a simple growth law is observed (in this case a parabolic growth law), we might tentatively assume that the reaction rate is given by an equation of the form

$$I = F(\phi) t^{-1/2}$$
 [3]

where  $F(\phi)$  is some function of the overpotential.

Two methods based on this approach were used to investigate the oxidation and reduction of cadmium and silver in potassium hydroxide electrolyte. Using the first method, the fixed potential method, we measure as a function of time the current required to maintain oxidation at a constant overpotential. We find that after sufficient time has elapsed the current and time are related by an equation of the form of Eq. [3]. Thus once it is established that the oxide grows according to a parabolic growth law, we interpret  $F(\phi)$  as a function relating the rate of the reaction to the overpotential.

In employing the second method, an electrode is first oxidized at a fixed rate (constant current) until it becomes passive. This state of the electrode corresponds to the onset of the  $t^{-1/2}$  current dependence observed using the fixed potential technique. The electrode is then oxidized or reduced at a rate such that  $\phi$  follows the form of a triangular wave. Simultaneously the current necessary to make the electrode potential follow this wave shape is recorded. Thus if the change in thickness of the oxide layer is negligible during the anodic or cathodic swing of  $\phi$ , measurements of I as a function of  $\phi$ yield  $F(\phi)$  vs.  $\phi$  directly. Both methods of measurement yield the result that for anodic values of  $\phi$ ,  $F(\phi)$  for cadmium electrodes has at least one maximum and often two. Furthermore, the overpotential



Fig. 1. Block diagram of control circuit used to maintain a given electrode overpotential.

observed during constant current oxidation (before passivity occurs) is equal to the potential corresponding to one of the maxima in the  $F(\phi)$  vs.  $\phi$ curve. Similar results were obtained for silver electrodes except that  $F(\phi)$  has only one maximum and this for cathodic potentials. The overpotential observed during constant current reduction of the silver electrode is equal to the potential corresponding to the maximum in  $F(\phi)$ .

#### Apparatus and Sample Preparation

A block diagram of the instrumentation developed to oxidize or reduce a test electrode at any desired overpotential is shown in Fig. 1. The circuit is designed so that any difference between the desired potential fed in at terminals T and the test electrode potential produces a flow of current through the test electrode via the auxiliary electrode. This current, either cathodic or anodic, causes a change in the test electrode potential which reduces to zero the difference in potential between the test and input potential.

Control of the electrode potential is achieved by converting the difference potential by means of a chopper (Chopper I) to a 400 cps signal which is amplified and used to drive a power amplifier. The output of the power amplifier is fed into the output chopper (Chopper II) which is synchronized with the input chopper. Such synchronization leads to a direct current output which is fed back through the test electrode via the auxiliary electrode in such a direction that the difference potential is reduced to zero.

The potentiometer *P* is used to buck out the test electrode-reference potential. The reference used was a partially discharged nickel electrode from an Edison nickel-iron-alkaline storage battery. The current and potential were measured on a recording milliammeter and a self-balancing recording potentiometer. Using this circuit one can force the electrode to oxidize at a fixed potential and record the current as a function of time, or make the potential follow some predetermined function of time and record the current necessary to produce this potential variation. If the current through the test electrode does not exceed 25 ma, the circuit maintains the desired potential (either anodic or cathodic) to within  $\pm 0.2$  my.

The cells used in both the fixed and sweeping potential measurements were of conventional design. Nitrogen was bubbled through the electrolyte in the fixed potential cell to reduce the dissolved oxygen concentration and to provide stirring of the electrolyte.

The cadmium electrodes used in the fixed potential experiments were prepared by electroplating cadmium onto nickel plates whose dimensions were  $3.7 \times 5.2 \text{ cm}$ . The cadmium overlay was 0.005-0.01cm thick and completely covered the underlying metal. The electrodes were cleaned by washing and scouring, followed by an overnight reduction at a cathodic potential of 37.5 mv.

The electrodes used in the sweeping potential experiments on cadmium were made from spectrographically pure Johnson-Matthey cadmium rods which were rolled into sheets, from which were cut electrodes of dimensions 2.86 x 3.00 cm. The electrodes were mounted in an epoxy resin with only one side exposed to the electrolyte.

The following procedure was used prior to recording the sweeping potential data. First the electrode was electrolytically polished in phosphoric acid and washed in distilled water. It was then placed in the cell and reduced at a high current density (approximately 1 amp/cm<sup>2</sup>). Hydrogen was evolved over the surface until the electrolyte in the cell was thoroughly flushed with hydrogen. The cathodic current was turned off and the electrode was then oxidized at a fixed anodic current (1 ma/cm<sup>2</sup>). When  $\phi$  rose to 30 mv anodic, the current was turned off and the electrode was left to return to thermodynamic equilibrium. The electrode was then alternately oxidized and reduced so that  $\phi$  followed the form of a triangular wave. Simultaneously the current necessary to produce this potential variation was recorded.

Fixed Potential Data—Cadmium The electrochemical reaction studied was

$$Cd + 2OH^{-} \rightarrow Cd(OH)_{2} + 2e$$

This was established by analysis of the x-ray diffraction lines of the reaction product. No evidence of CdO was observed.



Fig. 2. Log I vs. log t curves for cadmium electrodes oxidized at fixed potential.



Fig. 3. The quantity  $It^{1/2}$  vs. t for cadmium electrodes oxidized at fixed potential. No oxide present initially.

A typical series of log current vs. log time curves are shown in Fig. 2. Each of these curves was obtained by starting with an oxide-free surface previously maintained overnight at a cathodic potential (37.5 mv) and then instantaneously switched to a predetermined anodic potential.

After an initial slow decay, the current for the  $\phi = 24.6$  and 36.0 mv runs begins to follow an equation of the form of Eq. [3]. At higher potentials (58 mv) the *I* vs. *t* curve has three portions. In the first portion the current decays slowly with time, in the second the current is proportional to  $t^{-1}$ , and in the third portion the current is proportional to  $t^{-1/2}$ .

The quantity  $It^{1/2}$  obtained from the data shown in Fig. 2 is plotted vs. t in Fig. 3. For each potential the product  $It^{1/2}$  tends toward a constant final value independent of time. This behavior follows directly from the  $t^{-1/2}$  decay of current which starts after sufficient time has elapsed. The quantity  $It^{1/2}$  for the  $\phi = 24.6$  mv run exhibits a number of steps. This is probably caused by cracking or shearing off of the oxide film which exposes unoxidized cadmium to the electrolyte, which then oxidizes anew, etc.

Data similar to those in Fig. 3 are shown in Fig. 4. These results were obtained by suddenly advancing the electrode potential to 36.0 mv after the electrode had oxidized at 24.6 mv until the current was proportional to  $t^{-1/2}$ . More oxide was grown at this potential until the current decay was again propor-



Fig. 5. Log I vs. log t for a cadmium electrode initially in the passive state. The electrode was  $2.8 \times 3.0$  cm with one side exposed to electrolyte.

tional to  $t^{-1/2}$ . The potential was then suddenly made more anodic and more oxide was grown, etc. These data show that when sufficient time has elapsed after the sudden rise in anodic potential the product  $It^{1/2}$ approaches a constant even if an initial oxide is present on the cadmium electrode. In this particular example  $It^{1/2}$  tends toward the same value obtained if no oxide was present initially.

The characteristic shape of the curves shown in Fig. 2 to 4 is a reproducible function of  $\phi$ , but the currents at equivalent times after application of anodic potentials were not generally reproducible. The curves shown represent some of the more reproducible runs.

Figure 5 is a plot of log I vs. log t obtained by the fixed potential method using electrodes which were first oxidized at constant current until the overpotential rose to 30 mv. (As the constant current overpotential rises to a value greater than 30 mv, the electrode rapidly approaches the passive state. Thus these electrodes for all practical purposes were in the passive state.) The current necessary to force the electrode to oxidize at a fixed potential is greater at 30 mv than at 97 mv. This is consistent with the fixed potential observations on electrodes not previously oxidized.

By fitting the *I* vs. *t* data in the  $t^{-1/2}$  portion of the curve to Eq. [3] a number of determinations of  $F(\phi)$  were made. Values of  $F(\phi)$  determined by this procedure are shown plotted vs.  $\phi$  in Fig. 6. Points obtained from additional *I* vs. *t* data not shown in this report are also plotted in this figure. The scatter of the points indicates the difficulty of achieving reproducibility from sample to sample, but qualita-



Fig. 4. The quantity  $It^{1/2}$  vs. t for cadmium electrodes oxidized at fixed potential. Oxide present initially.



Fig. 6.  $F(\phi)$  vs.  $\phi$  for cadmium obtained using the fixed potential method.



Fig. 7. Rate of oxidation and reduction of a cadmium electrode vs. overpotential obtained by the sweeping potential method.

tively the points show that  $F(\phi)$  increases with  $\phi$  to a maximum which lies between 18 and 40 mv. As  $\phi$  is increased to potentials beyond the maximum,  $F(\phi)$  decreases rapidly.

Thus fixed potential measurements on electrodes oxidized in a number of ways all indicate that in the final portion of the I vs. t curve the current is proportional to  $t^{-1/2}$ . This dependence of current on time corresponds to a parabolic growth law. Furthermore, besides being a function of time, the rate of growth is a peculiar function of potential which has a maximum for values of  $\phi$  between 18 and 40 mv. Because of the difficulty of forming reproducible electrode surfaces, the potential at which the rate is maximum cannot be determined with great precision by the fixed potential method. However, the data indicate that there is a potential at which the parabolic growth rate is maximum. This result is confirmed by data presented below.

#### Sweeping Potential Data—Cadmium and Silver

The problem of forming reproducible electrode areas is partially eliminated if one uses the sweeping potential method. This method yields  $F(\phi)$  vs.  $\phi$  directly, and all the data are recorded using only one area, i.e., that associated with a single electrode.

Figure 7 is a plot of I vs.  $\phi$  obtained using the sweeping potential method and is typical of the be-

havior of pure cadmium electrodes. There is at least one potential at which the rate of oxidation is maximum ( $\phi = 18 \text{ mv}$ ), and often the rate has a peak at  $\phi \approx 40 \text{ mv}$ . The rate of reduction is a monotonically increasing function of the overpotential. The data also show a trend toward an increased current density at equivalent potentials as the (OH<sup>-</sup>) concentration in the electrolyte increases. It is difficult to make a quantitative statement about effects of (OH<sup>-</sup>) concentration changes because of the problem of maintaining reproducible surfaces from electrode to electrode.

Additional data were obtained on cadmium electrodes by simply increasing  $\phi$  linearly with time with no subsequent reversal of potential. The data shown in Fig. 8 with  $F(\phi)$  normalized also show peaks at  $\phi = 18$  and  $\phi = 40$  mv. These curves, when compared with the data plotted in Fig. 6, indicate that both methods, i.e., either fixed or sweeping potential, lead to the result that the rate of oxidation of cadmium in alkaline electrolyte is a function of potential and this function has at least one maximum in the range of potential between  $\phi = 18$  and 40 mv. Comparison of Fig. 7 and 8 shows that when the electrode is forced to follow a cyclic variation of  $\phi$  the details of the *I* vs.  $\phi$  curves near the origin are altered, but the position of the maxima in  $F(\phi)$  are unaltered.

These are very important new results. They show clearly that the rate of oxidation of the cadmium electrode is a function of the overpotential, that there is a potential at which the rate is maximum, and that the rate is a multivalued function of the overpotential.

Figure 9 shows I vs.  $\phi$  data obtained using the sweeping potential method and electrodes containing 1 atomic % of indium alloyed with cadmium. These electrodes were  $1 \times 1$  cm in dimension and were also mounted in resin with one side exposed to the electrolyte.

The addition of indium to cadmium electrodes causes supression of the 20 mv peak and the appearance of an additional peak between 60 and 70 mv. The 40 mv peak in the anodic quadrant remains, but a peak in the rate of reduction, i.e., in the cathodic quadrant, is introduced. Thus an indium impurity can introduce new peaks in both the rate of oxidation and reduction and can eliminate peaks associated with the pure electrode.



Fig. 8.  $F(\phi)$  vs.  $\phi$  obtained by sweeping potential measurements.  $F(\phi)$  is normalized to its maximum value. The points represent values obtained in a number of different runs using sweep rates ranging from 4.7 to 22.8 mv/sec.



Fig. 9. Rate of oxidation and reduction vs. overpotential for a cadmium electrode containing 1 atomic % indium.



Fig. 10. Comparison of data for silver electrodes using either the overpotential,  $\phi$ , or the capacity, Q, as the independent variable. Q in coulombs vs.  $\phi$  is superimposed on the rate vs.  $\phi$  data by plotting both the rate of oxidation and capacity data on the ordinate.  $-\Phi$ —• reduced at 2 ma/cm<sup>2</sup>;  $-\Phi$ —• reduced at 10 ma/cm<sup>2</sup>.

The rate of oxidation and reduction of silver electrodes in KOH electrolyte vs. overpotential was also measured using the sweeping potential technique. The electrodes were plates  $1 \times 1$  cm cast from 99.98% pure silver and mounted in epoxy resin with one polished side exposed to the electrolyte. The studies were made on the reaction,

$$2 \text{ Ag} + 2 \text{ OH}^- \rightleftharpoons \text{Ag}_2\text{O} + \text{H}_2\text{O} + 2 e$$

Figure 10 is a plot of I vs.  $\phi$  data obtained using a silver electrode. (Constant current oxidation data discussed later are superimposed on this plot.) The rate of oxidation is a monotonically increasing function of overpotential, but a strong peak in the rate appears at 46 my in the reduction quadrant.

#### Comparison of Overpotential vs. Charge and Current vs. Overpotential Data

The results of constant current oxidation and reduction of a silver electrode are shown in Fig. 10. The overpotential is plotted as a function of the charge Q where Q = It. Q is now the independent variable. Superimposed on this plot is the I vs.  $\phi$ curve, where  $\phi$  is the independent variable, which shows that when reduced at constant current the silver electrode overpotential drops to the value corresponding to the maximum in the I vs.  $\phi$  reduction curve. The overpotential remains constant until all of the Ag<sub>2</sub>O is reduced to Ag.

A similar plot using cadmium as the electrode is shown in Fig. 11. The constant current anodic overpotential rises to a value which corresponds closely to the potential at the first peak in the *I* vs.  $\phi$  plots for pure cadmium. The constant current overpotential remains approximately constant at this value over a wide range of *Q*, but as  $\phi$  exceeds 20 mv,  $d\phi/dQ$  increases rapidly with  $\phi$  until the oxidation reaction ceases, and the electrode becomes passive. Thus it appears that there is some fundamental connection between the rate of oxidation as a function of overpotential and the constant current oxidation and reduction characteristics of the electrodes.

The results of the measurements are best summarized in Fig. 10 and 11. It is evident that the rate



Fig. 11. Comparison of data for cadmium electrodes using either  $\phi$  or Q as the independent variable. Q vs.  $\phi$  data (for oxidation only) is superimposed on the normal I vs.  $\phi$  plot by plotting both I and Q on the ordinate. Constant current oxidation was at 5 ma/cm<sup>2</sup>.

of oxidation or reduction of Cd and Ag electrodes is a function of  $\phi$  and that it is maximum at particular values of  $\phi$ . There is a connection between the values of  $\phi$  at which the rate of oxidation or reduction is maximum and the overpotential that the electrode seeks under constant current oxidation or reduction conditions. For example, the maximum rate of reduction of Ag<sub>2</sub>O to Ag occurs at  $\phi = 46.0$  mv and, if this electrode is reduced at constant current, the overpotential drops to 46.0 mv and remains constant until all of the Ag<sub>2</sub>O is reduced. Similarly one of the peaks in the rate of oxidation of cadmium occurs around 18 my which corresponds approximately to the constant current overpotential. As the potential rises above this value the electrode goes rapidly over into the passive state.

The constant current cathodic overpotential of the silver electrode agrees favorably with the value (0.04 v) obtained by Glicksman and Morehouse (2). Comparison of these data is probably legitimate because measurements of overpotential vs. current density on the Ag<sub>s</sub>O to Ag system (see Fig. 10) indicate that the overpotential is relatively insensitive to the current density. The value of the constant current overpotential observed by Rozentsveig, *et al.* (3) agrees favorably with our value as does the general shape of the  $\phi$  vs. Q curves.

#### **Discussion of Results and Conclusions**

The dependence of rate of oxidation on potential has been measured by two methods and both agree qualitatively. The fixed potential studies of cadmium indicate that if the current is proportional to  $t^{-1/2}$  the rate of oxidation is maximum for potentials between  $\phi = 18$  and 40 mv. The sweeping potential results show that the rate of oxidation of cadmium is maximum at two values of  $\phi$ , one at approximately 18 mv and the other at 40 mv, and that an impurity in the metal such as indium can influence the potential at which the rate is maximum. Thus the results from each method are in good agreement.

The fixed potential experiments show that after sufficient time has elapsed the rate of oxidation follows a parabolic growth law. A parabolic growth law is consistent with at least two hypotheses. One is that the necessary electron transfer process in the growth of Cd(OH)<sub>2</sub> occurs at the metal-electrolyte interface and that metal ion goes into solution and later precipitates on the metal as Cd(OH)<sub>2</sub>. The parabolic growth characteristic sets in when the precipitated oxide completely covers the metal except for small pores. The rate is then limited by transport of the Cd<sup>-2</sup> ion or an equivalent through the pores. As the oxide grows, the Cd<sup>+2</sup> ion path increases, thus causing a current proportional to  $t^{-1/2}$ . Muller (4) has advanced a theory of passivity based on this mechanism.

The other hypothesis is that the cadmium ion, or  $OH^-$  ion, moves through the oxide and that the electron transfer process occurs at the oxide-electrolyte interface. Using this hypothesis, the parabolic growth law sets in when the exchange currents associated with the metal-oxide and oxide electrolyte boundaries are large compared with the rate of growth so that the rate is limited only by transport through the oxide. As the oxide thickens, the resistance increases and the current required to maintain the imposed potential decreases, thus yielding a parabolic growth law.

The following experimental facts support the latter hypothesis, namely, that the oxide grows by transport of mass and electricity through the oxide and that the solution process is not relevant.

The observations of steps in the  $It^{1/2}$  vs. t curve (Fig. 5) are difficult to explain by any other mechanism than local cracking of an adherent solid oxide film which exposes a clean metal surface to the electrolyte for further oxidation. If the solution-precipitation process were relevant, there would be no way of developing strains necessary to cause cracking. Furthermore, if the solution-precipitation process were relevant, the overpotential would be a result of either a gradient in electrostatic potential or gradient in concentration of dissolving species in the pores connecting the metal to the electrolyte. Thus  $F(\phi)$  vs.  $\phi$  as determined by the fixed potential method would fit either the expression in Eq. [1] or Eq. [2]. Clearly it fits neither expression, indicating that the solution-precipitation process is not the relevant process in oxidation of cadmium.

We have also noticed that  $Cd(OH)_{z}$  formed by a precipitation process differs in color from that formed by electrochemical oxidation of cadmium. Electrochemically prepared  $Cd(OH)_{z}$  is yellow and we have observed that it is bleached white when exposed to x-rays. Precipitated  $Cd(OH)_{z}$  is white. Again it is difficult to explain (a) the difference in color of the two compounds formed (according to the solution precipitation process) the same way, and (b) presence of traps in a presumably precipitated compound which are bleached out by x-rays.

One additional fact supporting the solid-state hypothesis is related to the  $F(\phi)$  vs.  $\phi$  data. The effects observed using the sweeping potential technique are similar to those observed in oscillographic polarography (6). One then might conclude that the sweeping potential effects are purely polarographic in character. However, it is difficult to reconcile this

view with the fact of agreement in the rate of oxidation vs. overpotential data as determined by both the sweeping and fixed potential techniques. If one were observing only a polarographic effect, one would not observe a peak in  $F(\phi)$  vs.  $\phi$  using the fixed potential technique. The quantity  $F(\phi)$  would be a monotonically increasing function of  $\phi$  with no peaks. Thus the solution hypothesis is not consistent with the facts, and one is forced to the alternate, that of growth controlled by some solid-state mechanism.

Accepting the solid-state hypothesis the data so far not discussed are given the following tentative interpretation.

The 58-mv curve in Fig. 2 shows a continuous transition of the rate of oxidation from a  $t^{-1}$  to a  $t^{-1/2}$ dependence on the time. The  $t^{-1}$  dependence of the rate of electrochemical oxidation corresponds to the logarithmic growth law often observed in air oxidation processes. A logarithmic growth rate is a result of transport of ions through a compound or across an interface, either metal-metal oxide or metal oxide-electrolyte, caused by a large local electric field intensity such that there is no local thermodynamic equilibrium. Thus the 58-mv curve suggests that, for values of  $\phi$  in excess of the overpotential for maximum parabolic growth rate, ions are initially transported either through the hydroxide film or across an interface under nonequilibrium conditions and that, as the film thickens, the internal field is reduced until the ions come to local thermodynamic equilibrium at the interfaces and in the interior of the hydroxide thus yielding a parabolic growth law.

It is of interest to note that the rate-limiting step in the  $t^{-1}$  part of the curve could be transferred across either interface. If this is true, additional measurements of rate vs. time in the high overpotential region could lead to a determination of the exchange current at the relevant interface.

Again taking the solid-state view, the new  $F(\phi)$  vs.  $\phi$  curve (see Fig. 9) obtained by addition of indium to the cadmium electrode is also given the following tentative interpretation.

It is very probable that some indium becomes incorporated in the cadmium hydroxide lattice causing changes in the type and number of imperfections in the hydroxide. If this is true, the effects caused by indium suggest that the peaks are related to the type of imperfections in the cadmium hydroxide crystal.

If the growth of the hydroxide is via transport of mass and electricity through the hydroxide (as the evidence indicates), the dependence of rate on overpotential must then be related to the transport properties of the hydroxide subject to the boundary conditions imposed by the metal-hydroxide and hydroxide-electrolyte interfaces. Our results indicate that the boundary conditions are related to the electrode overpotential. A more detailed discussion of the implications of this result and an interpretation of the  $F(\phi)$  vs.  $\phi$  curves is in preparation and will be published later.

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#### The Stability and Solubility of AgO in Alkaline Solutions

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#### ABSTRACT

Silver oxide is stable in boiling water and decomposes but very little at room temperature in strongly alkaline solutions. The presence of Ag<sub>a</sub>O does not affect this stability, but the presence of unoxidized silver does increase the rate of decomposition. When AgO dissolves in strongly alkaline solutions the dissolved form is primarily AgO and Ag(OH)<sub>n</sub><sup>-</sup>. The standard free energy of formation of the latter is -85,380 cal/mole.

Silver (II) oxide, AgO, has been known for some time and is now available commercially. Various methods for its preparation have been reported as well as several studies of its properties. Yet, in spite of all this, there is still confusion as to the nature and characteristics of this substance. There is conflicting information on its crystal structure as well as its stability.

The work reported here is the result of a study that has been made of AgO to eliminate some of this confusion and to determine some physical chemical constants.

In general there are two methods for preparing AgO. One of these is the electrolytic oxidation of silver in alkaline solution, or of silver ion in acid solution. However, it is difficult to get a pure product by this method. Our studies of the electrolytic oxidation of silver in alkaline solutions have shown that it is very difficult to oxidize silver completely to AgO. Denison (1) indicates that unoxidized silver is always present. In the preparation of the oxide by oxidation in acid solutions it is difficult to remove the last traces of anion.

The other method of preparation uses chemical oxidizing agents on silver ions. Various oxidizing agents have been suggested, e.g.,  $MnO_4^-$ ,  $S_2O_8^{--}$ , and ozone, but potassium persulfate in strongly alkaline solutions apparently gives the purest product (2, 3). In our work we used either a product prepared by this method or a commercially available material.

#### Experimental

Three types of analyses were performed on each batch of material to determine its purity. Samples of AgO were analyzed for oxygen content by heating to drive off oxygen; for silver by the Volhard method; and for oxidizing power by treating with KI and titrating the liberated  $I_2$  with thiosulfate (4). These analyses indicated that the material was always better than 97%, and usually closer to 99% AgO.

In the solubility measurements, the mixtures were quickly filtered through sintered glass filtering crucibles and acidified with HNO<sub>8</sub> to reduce  $Ag^{++}$  to  $Ag^{+}$  (4, 5). The sample was then titrated potentiometrically using a KI reagent and a silver electrode. The reference electrode was a saturated calomel electrode. The same precautions and techniques were used as are described in reference (6).

The KOH solutions were prepared by dilution of a stock solution to which some  $Ba(OH)_2$  had been added to remove carbonate.

X-ray diffraction patterns were obtained from a plane surface of the material made by pasting the sample on a platinum screen. A Norelco x-ray unit was used. The radiation was produced by a copper cathode, and a nickel foil served as a filter.

#### Results

X-ray diffraction patterns.—Schwab and Hartmann (7) prepared AgO by several different methods and, in general, obtained the same x-ray diffraction pattern for each preparation. However, a somewhat different pattern was obtained from a sample prepared by extensive oxidation of silver with ozone, and from an oxide prepared by anodizing silver nitrate between platinum electrodes and then boiling the product in water. These latter patterns were also obtained by others (8) from similarly prepared oxides. This difference in x-ray patterns indicates a





Fig. 1. X-ray diffraction patterns for AgO: (a) commercially available AgO; (b) AgO formed by anodizing Ag in KOH solutions; (c) AgO formed as in (b) but containing excess oxygen, AgO<sub>1.17</sub>; (d) most AgO specimens prepared by Schwab and Hartmann (7); (e) AgO prepared by extensive ozonization of Ag (7); (f) AgO prepared from product obtained by anodizing AgNO<sub>8</sub> (7, 8).

difference in structure. Samples prepared by these latter two methods have often been suspected of containing  $Ag_{z}O_{a}$  (9). It is possible that some such substance is formed and, being unstable, readily loses oxygen giving, in effect, AgO with somewhat larger lattice parameters.

Much of the work that has been reported on AgO has been based on a study of samples prepared by anodizing silver nitrate. Since such a sample has a different x-ray pattern than the AgO prepared by other methods, it is possible that its properties are also different. The oxides used in our work gave x-ray patterns similar to those of most of the preparations studied by Schwab and Hartmann. This pattern is also obtained from the AgO prepared by the electrolytic oxidation of silver in KOH solutions, Fig. 1. The relative intensities of these lines are not necessarily comparable since some of these patterns were obtained from powders and others from a plane surface.

Stability in aqueous solutions.—Since AgO is a strong oxidizing agent, it is possible that it may be unstable in water. However, reaction [1] is not

$$4AgO + 2H_2O \rightarrow 4Ag^+ + 4OH^- + O_2 \qquad [1]$$

thermodynamically spontaneous. Jirsa, *et al.* (4) studied this by placing AgO in boiling water and observed that the extent of decomposition of AgO increased with the amount of water used. Their explanation was that the decomposition continued until

Table II. Effect of boiling AgNO<sub>8</sub> on AgO

Solution	% AgO after boiling
H <sub>2</sub> O	97.6
0.1N AgNO <sub>3</sub>	95.6
0.5N AgNO3	94.2
1.0N AgNO <sub>8</sub>	92.3
2.0N AgNO <sub>3</sub>	88.3

the water was saturated with AgOH. However, it is possible that the AgOH could precipitate as Ag<sub>2</sub>O, and thus the decomposition of AgO by water would continue. The extent of decomposition would then depend on the time of boiling rather than the amount of water used.

In our attempt to test this, samples of AgO were placed for 1.5 hr in varying amounts of boiling water. The purity of the samples was determined iodometrically (4). There was no decomposition of AgO with such treatment (see Table I). In fact, the boiling water appears to purify the samples somewhat. It should be noted here that the oxide used by Jirsa and co-workers was prepared from the material produced by the anodization of a AgNO<sub>s</sub> solution.

In another test, samples of AgO were placed for 1.5 hr in boiling solutions of AgNO<sub>s</sub>. Here there was a marked effect on the AgO, Table II. This likely was due to the hydronium ion. The *p*H of the 2.0N AgNO<sub>s</sub> was 3.5. AgO does decompose in acid solutions (4, 5). The  $\Delta F^{\circ}_{zee}$  for reaction [2] is

$$AgO + 4H^{+} \rightarrow 4Ag^{+} + O_2 + 2H_2O$$
 [2]

about -54 kcal.

4

It is of interest to note whether this stability of AgO changes at still higher pH values. Portions of AgO were allowed to stand in KOH solutions at room temperature. Samples were taken at various time intervals to determine the extent of decomposition. Results are given in Table III. It is obvious that a very slight, but definite, deterioration takes place.

To test this stability further, samples of AgO were prepared by treating silver anodically in KOH solutions. After treatment these specimens were soaked in distilled water to remove KOH, dried in a stream of purified nitrogen, and then placed in a desiccator for at least a day. The weight gained in this process was assumed to be due to oxygen. One of these specimens was anodized for several weeks in order to get complete conversion to AgO. This was verified by x-ray diffraction pattern and by analysis. The other sample was anodized for a few days and, while the surface was converted to AgO, not all the Ag was

Table III. Stability of AgO in KOH solutions

Table I.	Effect	of	boiling	water	on	AgO
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Ml water	% AgO after boiling	Days
-		0
	97.7	1
25	97.8	3
50	98.1	7
300	98.3	14
500	98.2	60

% AgO after treatment				
13% KOH	7% KOH satu- rated with Ag <sub>2</sub> C			
97.6	97.6			
97.2	97.2			
96.9	97.5			
95.6	97.2			
96.5	97.3			
94.7	96.3			
	% AgO 13% KOH 97.6 97.2 96.9 95.6 96.5 94.7			

oxidized to AgO. The total composition could be represented by  $AgO_{\infty}$ . Both samples were kept in the dark in 30% KOH solutions for 4 months at room temperature. At the end of this time the pure sample had lost 2% of its weight. The amount that could have dissolved would have been only about 0.06% of the original weight. The x-ray diffraction pattern of the surface showed only lines of AgO. Hence any appreciable amount of Ag<sub>2</sub>O that formed did not remain on the surface of the electrode. Some may have been shed by the electrode. There was a small amount of dark colored material at the bottom of the test tube when the sample was finally examined.

At the end of the 4 months the  $AgO_{0.88}$  had lost only about 0.3% by weight, but this represented all the AgO there was on that electrode since the x-ray diffraction patterns showed that the surface had been completely converted to Ag<sub>2</sub>O. Measurement of the potential of this electrode vs. a zinc electrode showed the presence of AgO at the end of 2 months.

These results indicate that pure AgO does decompose slightly even in the more concentrated KOH solutions. This decomposition may be due to the presence of local cell action, with a potential of about 200 mv.

$$2 \text{ OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{ O}_2 + 2e \qquad E^\circ = -0.4 \text{ v}$$
$$2\text{AgO} + \text{H}_2\text{O} + 2e \rightarrow \text{Ag}_2\text{O} + 2 \text{ OH}^- \qquad E^\circ = +0.6 \text{ v}$$

This decomposition of AgO would be hastened by the presence of impurities such as Ag. However, at room temperature even this process takes place slowly, as indicated by the very slight decomposition of the AgO<sub>0.20</sub> preparation over a period of time.

It is possible that  $Ag_*O$  may decompose AgO catalytically, but there was no evidence for this even in boiling solutions of KOH, Fig. 2.

Solubility in KOH solutions.—The solubility of AgO in KOH solutions was measured at  $25^{\circ}$ C. The samples were allowed to equilibrate for at least 2 days although later work showed that equilibrium was reached in a few hours. Some of the results are given on Fig. 3. The solubility is a function of the OH<sup>-</sup> ion concentration. This indicates that the AgO dissolves by reacting with the OH<sup>-</sup> ions. So far as



Fig. 2. Effect of boiling solutions of KOH on AgO: 0, 7.5% KOH; •, 7.3% KOH saturated with Ag\_2O; x, 14.1% KOH.



Fig. 3. Solubility of AgO in KOH solutions at 25°C

comparison can be made, these values are the same as those for Ag<sub>2</sub>O (6). This is striking because ordinarily the higher valence oxide is more acidic.

Results obtained in more dilute solutions were treated to determine equilibrium constants for the formation of certain ions (10). Assume the following equilibria in solution.

$$AgO + H_2O \rightleftharpoons Ag(OH)_2$$
 [3]

$$AgO + OH^- + H_2O \rightleftharpoons Ag(OH)_{a^-}$$
 [4]

$$AgO + 2OH^{-} + H_2O \rightleftharpoons Ag(OH),^{--}$$
 [5]

The total solubility, S, then can be expressed as

$$S = M_{Ag0} + M_{Ag(OH)_3^-} + M_{Ag(OH)_4^{--}}$$
[6]

or

$$S = M_{\rm Ago} + K_2 M_{\rm OH^-} + K_3 (M_{\rm OH^-})^2 / [y \pm (1-1)]^2 \quad [7]$$

where  $K_z$  is the equilibrium constant for reaction [4] and  $K_s$  for reaction [5], the activities of AgO and H<sub>2</sub>O being taken as unity. If now a plot of S vs.  $M_{\text{OH}^-}$  is made, it is evident from equation [7] that the extrapolated value is  $M_{\text{AgO}}$  or  $M_{\text{Ag(OH)}_2}$ . Such a plot is shown on Fig. 4. The extrapolated value is 0.27 x 10<sup>-5</sup>M.



Fig. 4. Plot to determine value of  $M_{Ag0}$  and  $K_2$ 

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Rearranging equation [7]

$$(S - M_{\rm Ago})/M_{\rm OH^-} = K_2 + K_3 M_{\rm OH^-}/[y \pm (1-1)]^2$$
 [8]

Plotting the left hand member vs.  $M_{\text{oH}^-}$  and extrapolating now gives the value of  $K_2$ . This is shown on the upper portion of Fig. 4. The value for  $K_2$  is 17 x 10<sup>-5</sup>. Since this plot is parallel to the base line, the value of  $K_3$  is zero. Consequently, the dissolved form consists of AgO or Ag(OH)<sub>2</sub> and Ag(OH)<sub>3</sub><sup>-</sup>. Using the same technique the concentration of AgOH<sup>+</sup> is shown to be negligible.

$$AgO + H_2O \rightleftharpoons AgOH^+ + OH^-$$
 [9]

A similar treatment of the data of Johnston, *et al.* (6) shows the dissolved form of Ag<sub>z</sub>O in alkaline solutions to be Ag<sub>z</sub>O or AgOH and Ag(OH)<sub>z</sub><sup>-</sup>. The value of the equilibrium constant for the formation of the latter is  $3.6 \times 10^{-8}$ . Thus, although the total solubility of Ag<sub>z</sub>O and AgO in alkaline solutions is practically the same, the concentration of Ag(OH)<sub>z</sub><sup>-</sup> is greater than that of Ag(OH)<sub>z</sub><sup>-</sup>.

Since  $K_{zee}$  for reaction [4] is  $1.7 \times 10^{-4}$  the value of  $\Delta F_{zee}^{\circ}$  for this reaction is +5150 cal. Using accepted values for the free energy of formation of H<sub>2</sub>O and OH<sup>-</sup>, and +3615 cal/mole for AgO (11),  $\Delta F_{zee}^{\circ}$  for Ag(OH)<sub>s</sub><sup>-</sup> is -85,380 cal/mole. Likewise,  $\Delta F_{zee}^{\circ}$  for Ag(OH)<sub>z</sub><sup>-</sup> is -57,065 cal/mole.

The rate of solution of AgO in KOH solutions was also studied. This was done by stirring the KOH solutions with solid AgO and analyzing samples of the solution for dissolved AgO. This solubility passes through a rather sharp peak, Fig. 5. This has been observed by others also (12). A similar phenomenon has been noted in perchloric acid (13). It was suggested that this could be due to a solid phase transition. This is a possibility, although x-ray diffraction measurements gave no difference in patterns. Nor is this phenomenon due to a decomposition of AgO. The residue left after allowing AgO to stand in contact with the KOH solutions for several days was ana-



Fig. 5. Rate of solubility of AgO in 4.75M KOH at room temperature.

lyzed iodometrically, and there was no evidence of decomposition. The residue showed as much oxidizing ability after standing as before. If this peak were due to a reaction such as [10] then the

$$Ag(OH)_{3} \rightarrow 2Ag_{2}O + O_{2} + 4OH^{-} + 4H_{2}O \quad [10]$$

residue would gradually change from AgO to Ag<sub>2</sub>O. This reaction is thermodynamically possible, but neither weight measurements, analysis, nor x-ray diffraction patterns indicate that this or similar reactions take place unless, e.g., metallic silver is present. If this peak is due to a phase transition, e.g.,

AgO (A) + 
$$H_2O$$
 +  $OH^- \rightarrow Ag(OH)_3^-$  [11]

$$Ag(OH)_{3} \rightarrow AgO(B) + H_{2}O + OH^{-}$$
 [12]

it is a rapid transition and one not detected by our x-ray diffraction measurements. Furthermore, this peak was observed with samples of AgO obtained by treating AgNO<sub>3</sub> with  $K_2S_2O_3$  in a strongly alkaline solution, so it is unlikely that further contact with alkaline solutions would cause such a phase change.

It is possible that this peak in the solubility curve is due merely to a time lag necessary for a reaction such as [12] to take place and thus some time is necessary before solubility equilibrium is truly established.

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## Investigation of the Electrochemical Characteristics of Organic Compounds

#### III. Nitroalkanes

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#### ABSTRACT

A theory based on the electron density in the vicinity of a reducible nitro group which had been used to explain the effect of substituent groups and their position on the operating potential of aromatic nitro compounds has been extended to the nitroalkane compounds. The high theoretical ampere-minute capacity of the nitroalkane compounds, along with their high operating potentials, show these compounds to have considerable promise for use as cathode materials in primary cells.

Previous studies (1-3) of the electrochemical characteristics of organic N-halogen, aromatic C-nitroso, and aromatic nitro compounds have suggested the use of these materials as cathodes in primary cells because of their high theoretical ampere-minute capacities and practical operating potentials.

The performance characteristics of dry cells containing aromatic nitro and C-nitroso compounds as cathodes coupled with a magnesium anode and a magnesium bromide electrolyte have been described in previous papers (4, 5). These cells have many performance characteristics superior to those of existing commercial dry cells.

On the basis of these studies, the most promising class of organic cathode materials appears to be the aromatic nitro compounds because of their high theoretical ampere-minute capacity, both on a weight and volume basis. Since the aromatic nitro compounds represent only one class of a large number of organic compounds, extensive studies were made of the electrochemical characteristics of other organic nitro compounds. This paper deals with the work on the nitroalkanes.

#### Apparatus and Technique

Because of the irreversible nature of the electrode reaction and polarization effects encountered during current flow, the electrochemical characteristics of many inorganic and organic compounds often cannot be predicted by thermodynamic calculations and a knowledge of their physical and chemical properties. A technique, previously described by the authors (6), has been used to measure the operating potential during current flow and the coulombic capacity of various nitroalkane compounds. This technique consists in discharging at a constant current, in a large volume of electrolyte, a 0.5-g<sup>-1</sup> sample of the nitroalkane cathode material mixed with 0.05 g of Shawinigan acetylene black. The change in cathode potential with time was measured with a L&N Type

<sup>1</sup>Liquid compounds were tested by mixing 0.5 ml of the compound with Shawinigan acetylene black, discharging the resultant mix at the required rate, and making half-cell potential measurements in the usual manner. K potentiometer using a saturated calomel, reference electrode. The measured potentials were corrected for the IR drop associated with the apparatus and electrolyte by means of an oscillographic technique (7).

All half-cell potential data reported in this paper are referred to the normal hydrogen scale and include a liquid junction potential, which in most cases is small and can be neglected.

For most of the measurements an aqueous magnesium bromide electrolyte and a magnesium anode were used, while, in studying the effect of *p*H on potential, a zinc anode was employed with the acidic NH<sub>4</sub> Cl-ZnCl<sub>2</sub>-H<sub>2</sub>O and basic NaOH-H<sub>2</sub>O electrolytes.

#### Effect of Substituted Groups on the Electrode Potential of Nitroalkanes

#### **Experimental Results**

Presented in Fig. 1 are half-cell discharge curves for nitrobenzene and some low-molecular-weight nitroalkane compounds, discharged at a rate of 0.030amp/ml of cathode material in a 250 g/l MgBr<sub>2</sub>· $6H_2O$ electrolyte. It is seen that these simple primary nitroalkane compounds operate at lower potentials than nitrobenzene under these conditions of discharge. The latter finding is in general agreement



Fig. 1. Cathode potential of various nitroalkane compounds discharged in 250 g/l MgBr<sub>2</sub>·6H<sub>2</sub>O electrolyte at a rate of 0.030 amp/ml.





Fig. 2. Effect of substituted groups on the cathode potential of 2-nitropropane discharged in 250 g/l MgBr<sub>2</sub>· $6H_2O$  electrolyte at a rate of 0.030 amp/ml and 0.030 amp/g.

with polarographic data (8) obtained from these compounds over a wide range of pH values.

To test the effect of substituted groups on the electrode potential of the nitroalkane compounds, some 2-substituted 2-nitropropane derivatives were discharged in the MgBr<sub>2</sub> electrolyte. From the data presented in Fig. 2, it is seen that those compounds having electron-repelling groups such as  $-CH_s$ , and  $-C_2H_s$ , substituted in the 2-position of 2-nitropropane operate at lower potentials than the parent compound, while a compound such as 2, 2-dinitropropane, with a strongly electron attracting  $-NO_2$  group in the 2-position, operates at a potential 0.25 v higher than 2-nitropropane.

In Fig. 3 are presented discharge data for a series of chloronitropropane isomers discharged at a rate of 0.030 amp/ml in the 250 g/l MgBr<sub>2</sub>· $6H_2O$  electrolyte. As with the nitroaromatic compounds (2), the position as well as the type of substituted group



Fig. 3. Effect of the position of a substituted chloro group on the cathode potential of 1-nitropropane discharged in 250 g/l MgBr<sub>2</sub>·6H<sub>2</sub>O electrolyte at a rate of 0.030 amp/ml.



Fig. 4. Effect of the addition of successive chloro groups to a nitro-carbon atom of a nitroalkane compound discharged in 250 g/I MgBr\_2·6H\_2O electrolyte at a rate of 0.030 amp/ml.

appears to have a pronounced effect on the operating potential of nitroalkane compounds as evidenced by the progressively higher potentials obtained when the electron attracting -Cl group is successively substituted in the 3-, 2-, and 1-position of 1-nitropropane. The effect of the -Cl group in raising the potential of 1-nitropropane is seen to be appreciable only for the 1- and 2-positions, having very little effect when substituted in the 3-position.

The addition of a second and third -Cl group to a primary nitro carbon atom raises the operating potential of a nitroalkane compound still higher, as evidenced by the discharge curves in Fig. 4 for the various mono-, di-, and tri-chloronitroalkane compounds. It is interesting to note that, although the potential increases with each succeeding chloro addition, the potential increases at a decreasing rate, the increase being approximately 0.25-0.30 v for the



Fig. 5. Effect of the addition of successive nitro groups to a nitro-carbon atom of a nitroalkane compound discharged in 250 g/I MgBr\_2.6H\_2O electrolyte at a rate of 0.030 amp/ml.



Fig. 6. Cathode potential of various bromo and chlorodinitroalkane compounds discharged in 250 g/l  $MgBr_2 \cdot 6H_2O$  electrolyte at a rate of 0.030 amp/ml.

addition of the first -Cl group, 0.18-0.20 v for the second, and 0.03-0.12 v for the addition of a third chloro group to a dichloronitro compound.<sup>2</sup>

The effect on potential of adding successive  $-NO_2$ groups to a nitro carbon atom is shown in Fig. 5 where it is seen that the potential of the various nitroalkane compounds increases with each succeeding addition of a  $-NO_2$  group. The increase in potential due to this strongly electron attracting group is greater than that found for the -Cl group, as evidenced by the considerably higher cathode potential of tetranitromethane compared to that of trichloronitromethane.

In Fig. 6 are presented discharge data for two pairs of bromo- and chlorodinitroalkane compounds, discharged at a rate of 0.030 amp/ml in 250 g/l MgBr<sub>2</sub>·6H<sub>2</sub>O electrolyte. Under these conditions of discharge the bromodinitroalkane compounds operate at potentials 0.1 v higher than those of the corresponding chlorodinitroalkane compounds.

#### Discussion

The cathode potential of aromatic nitro compounds has been shown to be dependent on the type and position of the substituent group or groups on the ring (2). This has been explained on the basis of the electron distribution in the molecule. For example, in substituted nitrobenzenes, the introduction on the ring of electron-attracting groups, such as -CHO, -CN, and -Cl, decreases the electron density in the vicinity of the nitro group, thus increasing its affinity for electrons and facilitating its reduction. Conversely, electron-repelling groups such as -CH<sub>3</sub>, -OH, and -NH<sub>2</sub> increase the electron density around the nitro group, thus decreasing its affinity for electrons, resulting in compounds which are more difficultly reduced, i.e., with compounds having a lower cathodic discharge potential than the parent nitrobenzene.

The data presented in Figs. 2-5 also can be explained on the basis of the same theory. For example, it is seen from Fig. 2 that the effect of substituted electron attracting and electron-repelling groups on the potential of a nitroalkane compound during current flow is similar to that found for the nitrobenzene compounds. Further, the increase in potential due to the addition of a  $-NO_s$  group to the nitro-carbon

atom of a nitroalkane is greater than that found for the addition of a  $-NO_2$  group to the para, meta, or ortho position of nitrobenzene. This is attributed to the fact that, for the nitroalkane compound, the substituted  $-NO_2$  group is directly on the carbon atom containing the reducible nitro group, while for nitrobenzene such a grouping is impossible, and the effect of a nitro group must be transmitted through the ring carbon atoms.

By the same reasoning, one would expect the effect of an electron-attracting chloro group on the potential of a nitroalkane compound to diminish rapidly as saturated hydrocarbon groups are interposed between it and the  $-NO_2$  group. The discharge curves in Fig. 3 for a series of chloro-nitropropane isomers bear out this reasoning. This same effect is operative for a wide variety of other organic reactions (9, 10).

Similarly, the cathode potential of a nitroalkane compound can be increased by the addition of successive electron-attracting groups to the nitro-carbon atom. The effect of each substituted group is to lower the electron density in the vicinity of the reducible nitro group, thus increasing its affinity for electrons and facilitating its reduction. This type of behavior is illustrated by the discharge curves presented in Fig. 4 and 5 for the various mono-, di-, and tri-chloronitro, and the mono-, di-, tri-, and tetranitroalkane compounds.

It has been shown previously that substituted chloro groups raise the cathode potential of nitroalkane compounds. This is in accord with theory. However, contrary to theory, the data in Fig. 6 show that bromo substituted compounds operate at higher potentials under current drain than their corresponding chloro compounds. The reason for this is not known.

As with the aromatic nitro compounds, it is recognized that the reduction of nitroalkane compounds involves the acceptance of hydrogen ions as well as electrons, and either or both might be involved in the rate-determining step. However, the data presented in Fig. 2-5, can be explained readily on the basis of a rate-determining electron transfer step.

#### Coulombic Capacities and Operating Potentials of Solid Nitroalkane Compounds

Tabulated in Table I are theoretical capacity and electrode efficiency data for some nitroalkane compounds compared with a few aromatic nitro compounds and two of the cathode materials now used in commercial dry cells. The theoretical capacities of the nitro compounds were computed by means of Faraday's Law, with the assumption that each nitro group is reduced to the amino stage, with a corresponding 6-electron change.

It is seen that the listed nitroalkane compounds have theoretical ampere-minute capacities per unit of weight approximately 2 to 10 times those of manganese dioxide and mercuric oxide. The capacities of some of these nitroalkane compounds are comparable to those of the aromatic nitro compounds. As with the aromatic nitro compounds, the low densities of the nitroalkane compounds result in a greatly reduced theoretical capacity advantage over the in-

<sup>&</sup>lt;sup>2</sup> In making this comparison, it is assumed that the operating potentials of comparable chloronitroalkane derivatives, such as 1, 1-dichloro-1-nitroethane and 1, 1-dichloro-1-nitropropane, are approximately the same.

Table I. Theoretical capacities and electrode efficiencies of various cathode materials

Cathode	Physi- cal state	Theoretical capacity, amp-min/g	Electrode efficiencies, %
Conventional dry cell catho	de mate	rials	
Manganese Dioxide	Solid	18.5	66†
Mercuric Oxide	Solid	14.9	70
Aromatic nitro compounds			
Nitrobenzene	Liquid	78.4	
m-Dinitrobenzene	Solid	115	77
1, 3, 5-Trinitroben- zene	Solid	136	—
Nitroalkane compounds			
2-Nitropropane	Liquid	109	
2, 2-Dinitropropane	Waxy solid	144	
Tetranitromethane	Liquid	196	-
2, 4, 6-Trichloro-2, 4, 6-trinitroheptane	Solid	89.3	32
4-Bromo-4, 4-di- nitrobutyric acid	Solid	75.1	36
1, 1, 3, 3-Tetra- bromo-2, 2-di- methyl-1, 3-di- nitropropane	Solid	40.4	50
1, 1, 3, 3-Tetra- chloro-2, 2-di- methyl-1, 3-di- nitropropane	Solid	64.3	48
1, 1, 4, 4-Tetra- bromo-1, 4-di- nitrobutane	Solid	41.7	52

\* Efficiency calculation based on a -0.40 v cut off. † Efficiency calculation based on an 85% MnO<sub>2</sub> content.

organic compounds, when these cathode materials are rated on a volume basis (2).

The most attractive of these cathode materials is tetranitromethane, which has a theoretical ampereminute per gram capacity comparable to that of oxygen, and which, when coupled with a magnesium anode in a magnesium bromide electrolyte, results in a galvanic cell which operates at 2.0-2.1 v for the first reduction step.

Despite the attractive electrochemical properties of tetranitromethane and other nitroalkane compounds, many of these compounds are liquids or are unstable, and for that reason their use in primary cells would be limited. However, these liquid oxidizing agents have potential use as cathodes in continuous-feed cell systems and deserve serious consideration for this application.

There are, however, a number of solid nitroalkane compounds available which, because of their high theoretical ampere-minute capacities and operating potentials, show considerable promise for use as cathodes in primary cells. Coulometric studies of some of these compounds in a magnesium bromide electrolyte are presented in Fig. 7-10, while the electrode efficiencies<sup>3</sup> of a few of these are given in Table I. The results were obtained by discharging a 0.5-g sample of the compounds at a constant current drain of 0.005 amp/g, and measuring the change in half-cell potential with time by the same technique as previously described.





Fig. 7. Half-cell potential studies of various nitro and dinitroalkane compounds discharged in 250 g/l  $MgBr_2 \cdot 6H_2O$  electrolyte at a rate of 0.005 amp/g.

#### Nitro and Dinitroalkane Compounds

The data presented in Fig. 7 illustrate the fact that an electron-attracting group must be attached to the carbon atom containing the reducible nitro group in order to get useful potentials from nitroalkane compounds. For the compound dimethyl 5,5-dinitro -2,8diaza -1,9-nonanedioate such a grouping is available, and the reduction of the nitro group takes place at a half-cell potential of 0.00 to +0.10 v.

The low operating potential of the "vic"-2,3-dinitro-2,3-dimethylbutane compound as compared to that of the "gem"'-dinitro compound is attributed to the diminished effect of the  $-NO_2$  groups on each other as saturated carbon groups are interposed between them, while the higher operating potential of 2-nitro-1-phenyl-1-propene as compared to other mononitroalkane compounds is believed to be due to the effect of the unsaturated double bond in lowering the electron density in the vicinity of the reducible  $-NO_2$  group.

Despite their practical operating potentials, the gem-dinitro and 2-nitro-l-phenyl-l-propene compounds have poor electrode efficiencies, as measured under these conditions of evaluation.

<sup>4</sup> The prefix "gem" denotes attachment of both nitro groups to the same carbon atom, while "vic" denotes attachment to adjoining carbon atoms.



Fig. 8. Half-cell potential studies of various halo-nitroalkane compounds discharged in 250 g/l  $MgBr_2 \cdot 6H_2O$  electrolyte at a rate of 0.005 amp/g.



Fig. 9. Half-cell potential studies of various halo-dinitroalkane compounds discharged in 250 g/l  $MgBr_{2}$ · $6H_{2}O$  electrolyte at a rate of 0.005 amp/g.

#### Halo-Nitroalkane Compounds

The high operating potential of 1-chloro-1-nitropropane (Fig. 3) prompted a search for structurally similar solid chloronitroalkane compounds, which in addition contain a high percentage by weight of the -NO2 group. Presented in Fig. 8, are data obtained on a number of such compounds, which were discharged at a rate of 0.005 amp/g in a MgBr, electrolyte. It is seen that both 2.6-dichloro-, and 2.4.6trichloro-2,4,6-trinitroheptane operate at potentials close to that of 1-chloro-1-nitropropane and give capacities of 30 amp-min/g to a -0.40 v cut off, these capacities being approximately twice the theoretical limit of the inorganic cathode materials. Although these compounds operate at slightly higher potentials than aromatic dinitro compounds such as m-dinitrobenzene, the high electrode efficiency of the latter compound (77%) makes it a more attractive cathode material than a compound such as 2,4,6-trichloro-2,4,6-trinitroheptane which operates at an efficiency of 32% and gives one-third the capacity of the aromatic dinitro compound in a MgBr<sub>2</sub> electrolyte.

Also included in Fig. 8 are discharge data for two compounds containing a N-NO<sub>2</sub> grouping. From a comparison of the discharge curves of 2,6-dichloro-



Fig. 10. Half-cell potential studies of various dihalonitroalkane compounds discharged in 250 g/I  $MgBr_2$ ·  $6H_2O$  electrolyte at a rate of 0.005 amp/g.

2,4,6-trinitroheptane with 2,6-dichloro-2,4,6-trinitro-4-azaheptane, and 4-nitrazapentanoic acid with those of the primary nitroalkane compounds (Fig. 1), it would appear that those compounds containing a  $N-NO_{a}$  grouping operate at lower potentials than comparable compounds containing a C- $NO_{a}$  grouping. A similar type of relationship has been found for the operating potential of C-nitroso and N-nitroso compounds (3).

Halo-Dinitro and Dihalo-Nitroalkane Compounds

It has been shown previously that liquid nitroalkane compounds containing halo-dinitro and dihalonitro groups would operate at higher potentials than the halo-nitroalkane compounds which have just been considered. A number of solid nitroalkane compounds containing these groupings were evaluated as cathodes in a MgBr<sub>z</sub> electrolyte, and the results are presented in Fig. 9 and 10.

The halo-dinitroalkane compounds exhibit a twostep discharge curve, probably due to the reduction of one nitro group at a time. The most attractive of these compounds, 4-bromo-4,4-dinitrobutyric acid, operates at a half-cell potential of +0.4 to +0.5 v for the first reduction step and between -0.1 and -0.2v for the second step. The large difference in potential between the two stages of discharge is undesirable for many primary cell applications, and this together with their poor electrode efficiencies (36% for 4-bromo-4,4-dinitrobutyric acid) would limit the use of these halo-dinitroalkane materials as cathodes in primary cells at the present state of development.

The dihalo-nitroalkane derivatives, whose discharge curves are shown in Fig. 10, comprise another promising class of solid nitroalkane compounds. These compounds, which exhibit relatively flat voltage discharge curves, also operate at higher potentials than their corresponding halo-nitroalkane compounds.

The discharge curves of 1,1,3,3-tetrabromo- and 1,1,3,3-tetrachloro-2,2-dimethyl-1,3-dinitropropane further emphasize the fact that bromo-nitro compounds operate at higher potentials than their corresponding chloro-nitro compounds. Another interesting discharge curve is that of 2,5-dibromo-2,5-dinitrocylopentanone, because of the relatively high operating potential of this monobromo-nitro compound as compared to the dibromo-nitro compounds. The high potential of this compound is believed due to the effect of the electron attracting keto group in raising the potential of the adjacent Br-C-NO<sub>2</sub> groups.

Although the electrode efficiencies of the dihalonitro compounds are low (48-52%) compared to those of the aromatic nitro compounds (70-90%), they represent the best efficiencies which have been attained from any of the solid nitroalkane compounds. The poor electrode efficiencies of the nitroalkanes can be attributed either to the relative difficulty in completely reducing a nitroalkane to its corresponding amine, or to the fact that, under present conditions of discharge, the electrolytic reduction of the nitroalkane compound does not take place to the amine but to some intermediate stage. On the



Fig. 11. Half-cell potential studies of 1,1,4,4-tetrabromo-1,4-dinitrobutane and 1,1,3,3-tetrachloro-2,2-dimethyl-1,3-dinitropropane discharged in various electrolytes at a rate of 0.005 amp/g.

basis of the above study, no satisfactory statement can be made about either possibility, and additional study of the reaction mechanism is needed in order to resolve this problem.

A review of the literature revealed that the reduction of mononitroalkanes to primary amines may be effected with a wide variety of reducing agents under various conditions (11-13). Strong reducing conditions yield amines. Hydrogen and a catalyst (Pt, Pd) are most frequently used, but good yields of amine have been reported from reductions by metals and acids, as well as by electrolytic methods. Mild reduction of primary and secondary nitroalkanes with zinc and acetic acid yields aldoximes and ketoximes, respectively, while still milder reducing conditions such as zinc in water or aqueous NH,Cl yields the N-alkylhydroxylamine.

Additional coulometric studies of 1,1,4,4-tetrabromo-1,4-dinitrobutane and 1,1,3,3-tetrachloro-2,2dimethyl-1,3-dinitropropane in electrolytes of different *p*H are presented in Fig. 11. It is seen that the cathode capacities of these compounds increase with decreasing *p*H of the electrolyte, especially when taken to a low end potential. However, the capacities obtained in the acidic NH<sub>i</sub>Cl-ZnCl<sub>2</sub> electrolyte are still considerably less than the theoretical capacities of these compounds when calculated on the basis of a 6-electron change per  $-NO_2$  group.

The poor capacities obtained from the nitroalkane compounds in the strongly basic NaOH electrolyte is



Fig. 12. AA-size dry cells discharged continuously through 4 and 50-ohm resistances at  $70^{\circ} \pm 2^{\circ}F$  (50% RH).

similar to that encountered for the aromatic dinitro compounds and could be attributed to the presence of side products which are formed by the condensation of the primary reduction products. In addition, nitroalkanes in the presence of alkaline reagents may undergo oxidation-reduction and extensive decomposition reactions, with a concommitant loss in cathode capacity.

It is interesting to note that the effect of pH on the operating potential of these nitroalkane compounds is very small, a relationship quite different than that found for the aromatic dinitro compounds (2). This type of behavior agrees with that found from polarographic studies, which show that the half-wave potentials of the nitroalkanes change only slightly with pH, while those of the nitroaromatics show a considerable variation with pH (8).

#### Experimental Dry Cell Data

Experimental dry cells containing 1,1,3,3-tetrachloro-2,2-dimethyl-1,3-dinitropropane and 1,1,4,4tetrabromo-1,4-dinitrobutane cathodes were assembled in the usual manner (4) using an impact extruded Mg AA-size can be composed of an AZIOA Dow Chemical Co. alloy, and a 500 g/l MgBr<sub>2</sub>· $6H_{2}O$ electrolyte. The cathode mix (weighing approximately 5 g) consisted of two parts by weight of the nitroalkane compound to one part by weight of Cabot experimental battery black.

The performance characteristics of these magnesium-nitroalkane AA-size dry cells on a 4- and 50-ohm continuous discharge test are shown in Fig. 12. Included for comparison are performance data for comparable size commercial Leclanché, and Mg/  $MgBr_s/MnO_s$  dry cells (14) of the type being developed by the Dow Chemical Company.

On the 4-ohm continuous discharge test, it is seen that the magnesium-nitroalkane cells are superior to the Leclanché cell both on the basis of minutes of service to specified end voltages, and operating voltage. Compared to the Mg-MnO<sub>2</sub> cell, the magnesium-1,1,4,4-tetrabromo-1,4-dinitrobutane cell operates at a higher voltage and gives comparable minutes of service to the inorganic cell.

On the lighter drain 50-ohm continuous discharge test, both organic cells give comparable hours of service to the Leclanché cell to a 0.90 v end point but are inferior to the Mg-MnO<sub>2</sub> cell in this respect. The organic cells, however, operate at higher voltages than the Leclanché cell on this test, while the magnesium-1,1,4,4-tetrabromo-1,4-dinitrobutane cell has a voltage comparable to that of the Mg-MnO<sub>2</sub> cell.

These results, while only representing the data obtained on two nitroalkane cathode materials, demonstrate the possible practical application of these materials in primary cells.

#### Summary

1. A theory based on the electron density in the vicinity of a reducible nitro group is presented which explains the effect of substituent groups and their position on the operating potential of nitroalkanes. For example, the effect of an electron-attracting chloro group on the potential of a nitroalkane diminishes rapidly as saturated hydrocarbon groups

are interposed between it and the nitro group. It is also seen that the addition of successive chloro or nitro groups to a primary nitro carbon atom increases the potential of the parent nitroalkane compound with each succeeding addition of the electron attracting group.

2. Coulometric studies in a MgBr<sub>2</sub> electrolyte indicate electrode efficiencies of 36-52% can be obtained from a number of solid nitroalkane compounds, assuming a 6-electron change per nitro group. The latter assumption is in doubt, however, since the reduction mechanism is not known.

Magnesium-nitroalkane dry cells have been 3 assembled, and the performance characteristics of these cells indicate that nitroalkane compounds show promise for use as cathodes in primary cells.

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#### Oxidation Studies on the Iron-Chromium-Aluminum Heater Alloys

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#### ABSTRACT

The oxidation behavior of three iron-chromium-aluminum alloys was studied using sensitive weight gain techniques. In addition, x-ray diffraction methods were used to determine the crystal structure and composition of the oxide films. The adhesion characteristics of the oxide film to the metal were tested by introducing strains into the metal oxide system during oxidation.

Rate studies show a change in rate for the three alloys near 900°C. Between 900° to 1050°C the rate of oxidation remained nearly constant; above 1050°C it increased again. X-ray diffraction studies suggest that a crystal structure transformation was occurring in the oxide. At 1050°C,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was the main oxide in the scale.

The parabolic rate law was used to interpret the rate data. Deviations occurred during the initial reaction period as a result of crystal structure transformations in the film. Heats of activation of 76 to 77 kcal/mole were calculated for the range 700°-900°C.

Strain oxidation studies showed the oxide scale on the high aluminum alloy to be less susceptible to damage than the lower aluminum content alloys. These studies were correlated directly with practical performance tests.

Thermodynamic analyses of the several types of solid-solid and solid-gas reactions were used to interpret the rate and structure studies. Preliminary design principles were proposed for heat resistant alloys.

Heater alloys have been characterized by three important properties: (a) high melting point, (b) high resistance to oxidation, and (c) good mechanical properties. For extreme service conditions, two types of alloys have been used: (a) Ni-Cr alloys of nominal composition 80% Ni and 20% Cr, and (b) Fe-Cr-Al alloys of nominal composition 20-25% Cr, 4-6% Al, balance Fe. Both alloy systems consist of a single phase with the Ni-Cr alloys having the austenitic structure and the Fe-Cr-Al alloys the ferritic structure.

The maximum operating temperature in the final analysis is limited by the alloy's solidus point. This is about 1440°C for the Fe-Cr-Al alloys and 1380°C

for the Ni-Cr alloys. Neither series of alloys can be used at temperatures near their solidus point as the rate of oxidation and scaling becomes excessively high and the mechanical properties become poor. At extreme temperatures the oxidation resistance of the alloy determines, in part, the usefulness of the alloy as a high-temperature material.

The oxidation resistance of metals has been related to the formation of lattice defects and the diffusion of cations, anions, and electrons through these defects (1,2). This picture, based on a uniform oxide film, is probably too simple as has been shown by the formation of oxide needles, whiskers, and platelets (3, 4) on the scale. These suggest that certain areas of the metal are much more reactive than the rest of the surface.

If the metal is oxidized under periodic temperature cycles or when subjected to stresses or to a strain, the oxide-metal interface may be damaged (5). As a result, the rate of oxidation increases. The oxidation resistance of the alloy for these conditions is governed not only by diffusion processes but also by the chemical and physical properties of the oxide, alloy, and oxide-alloy interface.

The objectives of this study are: (a) to determine the kinetics of the oxidation of three Fe-Cr-Al alloys as a function of time, temperature, and alloy composition, (b) to determine the effect of strain on the oxidation process, (c) to determine the crystal structure of the oxide scales, and (d) to interpret from the experimental observations and thermodynamic analysis the high heat resistance of the Fe-Cr-Al alloys.

Literature.—von Kantzow (6) first observed that the heat resistance of steels was improved by alloying with aluminum. A series of alloys of Fe-Cr and Al were developed and patented. Since 1932 these alloys have been manufactured under the name of Kanthal' alloys.

The heat resistance of Fe-Al and Fe-Cr alloys has been studied by several groups (7-12). Hauttman (7) showed the strong effect of increasing the Al content between 4 and 9% at 1000°C. Al<sub>2</sub>O<sub>8</sub> was found in the oxide layer on a 9.44% Al alloy. Scheil and Schulz (8) in a study of Cr-Al steels at 1200°C showed that the most oxidation resistant alloys were covered with a white aluminum oxide scale. At temperatures above 1000°C an Al content of greater than 4% was necessary to get a high degree of oxidation resistance. The high oxidation resistance properties and high electrical resistance suggested the use of Al-Cr steels for heater alloys. Ziegler (9) and Portevin, Pretet, and Jolivet (10) also noted the beneficial affect of adding Al to improve the oxidation resistance of steels.

The nature of the scaling process in the oxidation of steels containing Ni, Cr, and Al has been discussed by Krainer, Wetternik, and Carius (11). The loss by scaling was lowest for steel containing 24% Cr and 5% Al and having a scale of Al<sub>2</sub>O<sub>3</sub>. However, the resistance of the layer to scaling with temperature fluctuations was best for a  $Cr_2O_3$  scale and poorest for an Al<sub>2</sub>O<sub>3</sub> scale.

<sup>1</sup>Kanthal is a proprietory name for a series of heater alloys manufactured by Kanthal Corp., Stamford, Conn. The segregation of aluminum atoms in Al-Cr-Fe alloys toward the periphery is discussed by Sektova (12). Sektova also noted the strong effect of Al to improve the oxidation resistance of these alloys.

#### Experimental

The vacuum microbalance method has been described (13-15). In this study a microbalance of low sensitivity,  $4.39\mu g/0.001$  cm deflection, was used. A total weight change of about 7 mg could be measured with a sensitivity of  $1.10 \times 10^{-6}$  g. This low sensitivity microbalance together with the use of smaller specimens increased the range of the measuring system by a factor of 25.

A vacuum grade mullite furnace tube contained the sample. It was sealed directly to the Pyrex glass system. With the specimen in the furnace tube at 1100°C, a McLeod gauge pressure of  $3 \times 10^{-4}$  mm Hg was readily obtained in the system. The vacuum system and gas preparation system have been described (15).

The furnace temperature was controlled to about  $\pm 1.5$  °C. There was no evidence of a temperature gradient along the 2.25-cm specimen during oxidation.

Weight changes occurring during the reaction were followed in a semicontinuous manner by observing a pointer on a balance beam using a micrometer microscope. Readings of the balance were taken *in vacuo* before reaction at temperature, during the reaction in oxygen, and after reaction *in vacuo*. Weight changes due to reaction of carbon in the metal with the surface oxide and to vaporization of metallic elements from the alloy were small.

Specimens used in this study were three types of commercial heater alloys obtained from the Kanthal Corporation. Table I shows the approximate and spectroscopic analysis of the alloys and their ratings as heater alloys. The 0.025-cm thick specimens were prepared from 0.63 cm wide strips and had surface areas of about 2.25 cm<sup>2</sup>. Sample weight was about 0.1886 g. Sections of the strip were abraded starting with No. 1 polishing paper and finishing through 4/0 paper. To avoid oxidation, the last stage was carried out under purified kerosene. After abrading, the samples were cleaned with soap and water, distilled water, petroleum ether, and absolute alcohol, and stored in a desiccator.

Strain oxidation.-Earlier studies of the Ni-Cr series of alloys (5) and the studies of Krainer. Wetternik, and Carius (11) have shown that constant temperature studies cannot be used alone to evaluate the protective characteristics of a particular alloy if the alloy is subjected to stress or to a strain in its use. To give a more complete picture of the physical and chemical factors involved in high-temperature oxidation, a new test method called strain oxidation was developed. In this method the metal is oxidized to a given weight gain, removed from the balance system and strained 1-4% in a tensile machine. After cutting a smaller section of the sample free from grip marks, the specimen was placed in the balance system and re-oxidized. Rate calculations before and after strain were made on a 1 cm<sup>2</sup> basis. To achieve

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Table I. a. Approximate composition\* Fe-Cr-Al alloys (Kanthal Corporation)

Weight per cent

Alloy	с	Si	M	n Cr	Al	Co	F	e	Relative useful life at 1200°C
1	0.07	0.65	0.2	26 23.0	5.7	0.57	Bala	nce	175
2	0.06	0.74	0.2	27 22.4	5.1	0.59	Bala	nce	150
3	0.07	0.65	0.2	2 21.7	4.5	0.58	Bala	nce	100
			1	b. Spectroscopic analys	es† (Westingho	use)			
				Weight p	er cent				
Alloy	Мо	Ni	Cu	Zr	Pb‡	Sn	Mg	v	Ca
1	< 0.01	<0.1	~0.01	0.01-0.05	< 0.01	< 0.05	< 0.001	< 0.01	< 0.01
2	0.5 - 0.9	0.1-0.5	~0.01	Not detected	< 0.03	< 0.05	< 0.001	< 0.01	< 0.01
2	<0.01	<01	- 0.01	Not detected	20.01	20.05	20.001	20.01	20.01

\* Traces of other elements to improve oxidation resistance. † Tested for but not detected: Nb, Ta, Ti, and Ce.

t Erratic segregation.

a strain of 1% a stress corresponding to the yield point or greater was imposed on the sample.

X-ray diffraction method.—Filtered Cr K<sub>e</sub> radiation was used with a fine focus x-ray diffraction tube. The diffraction patterns were made at room temperature using a 9 cm Unicam camera.

Oxide samples were removed from the alloy by electrochemical stripping (16). After washing several times in distilled water, the oxide films were rolled on to small glass capillary tubes for mounting in the x-ray camera.

#### Results

The three alloys were oxidized at 600°-1100°C using an oxygen pressure of 7.6 cm Hg for a reaction



Fig. 1. Effect of temperature on oxidation Fe-Cr-Al alloy 1, 7.6 cm Hg of  $O_{2}$ , abraded through 4/0.



Fig. 2. Effect of temperature on oxidation of Fe-Cr-Al alloy 2, 7.6 cm Hg of  $O_2$ , abraded through 4/0.

time of 2 hr. Weight gain during reaction was calculated in units of micrograms per square centimeter.

X-ray diffraction analysis suggested that the oxides were largely  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>. Assuming  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and a surface roughness ratio of unity, a value of 54 was calculated for the relation between the oxide thickness in angstroms and the weight gain in micrograms per square centimeter.

Time and temperature.—Figures 1-3 show oxidation curves for the three alloys in the range 800°-1100°C. There was a rapid initial reaction rate in all curves, with the rate decreasing as the oxide film grows. No evidence was found for a linear rate law for the times studied. All of the oxides were grayishblack and were adherent to the alloy when cooled to room temperature.

Below 900°C the oxidation curves show a strong dependence on the temperature. However, between 900° and 1050°C, the rate was nearly constant for each of the alloys. Above 1050°C it increased again with temperature.

This nearly constant rate of reaction between  $950^{\circ}$  and  $1050^{\circ}$ C is of great interest and suggests that major structural changes were occurring in the alloy or in the oxide scale.

A comparison of the rate of oxidation of the three alloys at 1100 °C shows only minor differences in the amount of oxidation or in the final rate of oxidation. Practical performance tests of alloys in Table I show alloy 1 to be superior to 2 and 3.



Fig. 3. Effect of temperature on oxidation of Fe-Cr-Al alloy 3, 7.6 cm Hg of  $O_{2}$ , abraded through 4/0.





Fig. 4. Oxidation Fe-Cr-Al alloy 2, 1100°C, 7.6 cm Hg of  $O_2$ , abraded through 4/0, parabolic plot, A = 2.16 x 10<sup>-12</sup> (a/cm<sup>2</sup>)<sup>2</sup> sec <sup>-1</sup>.



Fig. 5. Oxidation Fe-Cr-Al alloy 2, 1000°C, 7.6 cm Hg of  $O_2$ , abraded through 4/0, parabolic plot, A = 0.695 x 10<sup>-12</sup>  $(a/cm^2)^3$  sec<sup>-1</sup>.

Parabolic rate law.-The parabolic rate law is useful in evaluating the nature of oxidation reactions even though deviations may occur, since the law is based on fundamental physical principles (1, 2). Physical and chemical changes occurring in the oxide film are noted as deviations from the rate law.

The equation states that  $W^2 = At + C$ . Here W is the weight gain, t is the time, and A and C are constants. Figure 4 shows a parabolic rate law plot at 1100°C for alloy 2. Agreement with the theoretical law was good except for the initial part of the reaction.

From 750° to 900°C the parabolic rate law constant increases during the first several hours of reaction over the initial value, while above and below this temperature range the parabolic rate law constant decreases with time. These effects also may be related to minor changes in the composition or physical structure of the oxide film. In the temperature range 900°-1050°C a major change occurred in the alloy or oxide film, since the temperature coefficient of the reaction was near zero. A change also occurs in the oxide film or alloy as a function of time for this temperature range. This was seen in the 1000°C parabolic rate law plot shown in Fig. 5. The parabolic rate law constant decreased rapidly during the first 60 min of reaction after which a nearly constant value was found.

Temperature dependence.—Figures 6 to 8 show plots of the logarithm of the parabolic rate law constant A vs. 1/T for the three alloys. Below 900 °C and continuous with the curve for the initial oxidation.



Fig. 6. Oxidation Fe-Cr-Al alloy 1, log A vs.  $1/T\Delta H =$ 76,900 cal/mole.



Fig. 7. Oxidation Fe-Cr-Al alloy 2, log A vs.  $1/T\Delta H =$ 76,900 cal/mole.

straight line relationship was observed. Between 900° and 1050°C the plots show the transition phenomenon already noted. The slopes of the  $\log A$  vs. 1/T plot and the absolute values of A for the three alloys were similar. Analysis of the slopes of Fig. 6-8 for alloys 1 and 2 shows heats of activation of 76,900 cal/mole and for alloy 3, 76,500 cal/mole. These are very high for oxidation processes.

#### Strain Oxidation

The several alloy specimens were oxidized at 900°C to form an oxide film of about  $44.7\mu g/cm^2$  or an estimated oxide thickness of 2410Å. After straining 2-4%, the specimens were re-oxidized at 900°C.

Figure 9 shows the results for a 2% strain for alloy 1. The oxidation curve after 2% strain was nearly

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Fig. 8. Oxidation Fe-Cr-Al alloy 3, log A vs. 1/T  $-\Delta H =$  76,500 cal/mole.



Fig. 9. Strain oxidation of Fe-Cr-Al alloy 1, 2% strain: a, 900°C, 7.6 cm Hg of  $O_{z_r}$  A= 3.55 x  $10^{-18}$  (g/cm<sup>3</sup>)²/sec; b, 900°C, 7.6 cm Hg of  $O_{z_r}$  after cooling, stretching 2% and reheating, A = 4.0 x  $10^{-18}$  (g/cm<sup>3</sup>)²/sec.

Figure 10 shows the strain-oxidation curve for alloy 1 for a 4% strain. A marked change in the course of oxidation was noted as a result of the 4% strain.

The usual effect of strain between the several oxide layers and the metal is flaking of the oxide with loss of protection of the metal (5). For heat resistant alloys 1-4% strain may not visually destroy the bonding between the oxide and metal but localized damage on a microscopic or submicroscopic level may occur which affects the rate of oxidation.

Some damage in the oxide or at the interface between metal and oxide has occurred as a result of 4% strain of alloy 1 as shown in Fig. 10. This damage was smaller than that observed on other alloys for the same amount of strain (5). Two types of damage are postulated to occur as a result of straining of the alloy. The first is a short-term damage which is rapidly repaired by further oxidation. The second is long-term damage. This damage involves an increase in the rate of reaction which continues over long periods of time. A comparison of the parabolic rate law constants before and after strain shows some



Fig. 10. Strain oxidation of Fe-Cr-Al alloy 1, 4% strain: a, 900°C, 7.6 cm Hg of O<sub>2</sub>,  $A=4.09 \times 10^{-13} \ (g/cm^2)^2/sec;$  b, 900°C, 7.6 cm Hg of O<sub>2</sub>, after cooling, stretching 4% and reheating,  $A=5.12 \times 10^{-13} \ (g/cm^2)^2/sec.$ 



Fig. 11. Strain oxidation of Fe-Cr-Al alloy 2, 2% strain: a, 900°C, 7.6 cm Hg of O<sub>2</sub>,  $A=3.40\times10^{-13}~(g/cm^2)^2/sec;$  b, 900°C, 7.6 cm Hg of O<sub>2</sub>, after cooling, stretching 2% and reheating,  $A=6.41\times10^{-13}~(g/cm^2)^2/sec.$ 

long-period damage for both 2 and 4% strains for alloy 1.

Figures 11 and 12 show the results of strain oxidation studies of alloys 2 and 3. Both alloys show shortand long-period damage resulting from a 2% strain. A comparison of the strain oxidation tests for alloys 1, 2, and 3 show alloy 1 to be superior. These results are in agreement with the useful life tests given in Table I. The useful life tests are temperature cycling tests and are used to evaluate heater alloys.

#### Crystal Structure Studies

Table II shows the results of crystal structure studies on 2-hr oxidation experiments for the three alloys and for the several temperatures. Crystal structure studies were made above and below the transition temperature region of  $1000^{\circ}$ C. The x-ray diffraction patterns showed sharp lines for all of the oxide scales studied.

Complete identification of all of the diffraction lines was not possible since the stripping process reTable II. Summary crystal structure studies Fe-Cr-Al alloys

Temp, °C	Alloy 1 Crystal structures	Temp, °C	Alloy 2 Crystal structures	Temp, °C	Alloy 3 Crystal structures
		850	$\alpha - Al_2O_3$	800	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
			s.a. $Cr_2O_3$		$Cr_2O_3$
			s.a. MnO		MnO
950	$\alpha - Al_{2}O_{3}$	950	$\alpha - Al_2O_3$	900	$\alpha - Al_2O_3$
	s.a.* Cr <sub>2</sub> O <sub>3</sub>		tr. $Cr_2O_3$		$Cr_2O_3$
	tr.† MnO				MnO
1050	$\alpha = A l_{2} O_{2}$	1050	$\alpha - Al_2O_3$	1050	$\alpha - Al_2O_3$
1000	s.a. g-Fe <sub>2</sub> O <sub>2</sub>				MnO
					tr. Cr.O.
	tr. spinel $a_o = 8.12$ Å		tr. spinel $a_o = 8.12$ Å		tr. spinel $a_o = 8.12$ Å

\* s.a. = small amount † tr. = trace.

moves carbides, nitrides, etc. from the surface layer of the alloy. As a result a number of extra reflections occur. Identification of the major oxide components was readily made. Oxides present in trace amounts were identified with less reliability by two or three characteristic reflections.

Alpha-Al<sub>2</sub>O<sub>8</sub> was the principle oxide found in all of the oxide scales shown in Table II. Cr<sub>2</sub>O<sub>8</sub> and MnO appear in the oxide scale at temperatures of 900°C and lower. The identification of MnO is open to some question since its diffraction pattern is nearly identical to those for NbC, NbN, and TaC (17). These compounds could conceivably be present in trace amounts in high-temperature alloys. Spectroscopic analyses of the alloys in Table I showed no evidence for Nb or Ta in the metal.

In the transition temperature zone the Cr<sub>2</sub>O<sub>8</sub> content of the oxide scale decreases. In addition, a spinel, probably FeO·Al<sub>2</sub>O<sub>8</sub>, appears in the oxide having a parameter of 8.12Å (17). These changes in oxide composition occur for all of the alloys.

Alloy 3 containing the lowest amounts of Al, Cr, and Mn shows the largest amount of MnO structure in the oxide scale. Alloy 3 also shows the largest amount of damage in the oxide in strain oxidation tests.

We conclude that crystal structure differences exist in the oxide scales of the three alloys as a result of minor differences in alloy composition. These



Fig. 12. Strain oxidation of Fe-Cr-Al alloy 3, 2% strain: a, 900°C, 7.6 cm Hg of O<sub>2</sub>,  $A = 3.29 \times 10^{-13} (g/cm^3)^3/sec;$ b, 900 °C, 7.6 cm Hg of  $O_{2}$ , after cooling, stretching 2% and reheating,  $A = 4.34 \times 10^{-18} \text{ (g/cm}^2)^2/\text{sec.}$  crystal structural differences affect the adhesion properties of the oxide as shown by the strain oxidation studies or by practical performance tests. These differences do not appreciably affect the rate of oxidation at constant temperatures above and below the transition temperature zone.

#### Thermodynamic Interpretation

Table III shows the principal types of reactions which may occur in the oxidation of Fe-Cr-Al alloys. These determine in part the constitution of the oxide scale formed at high temperatures. Precise calculations of the thermodynamic properties of the oxidation products necessitate consideration of the relative rates of attack of the several metals and interdiffusion processes in the alloy, as pointed out by Wagner (18) for a number of binary systems.

The thermodynamic evidence given below for most of these reactions assumes a standard state of unit activity for the component metals. For many of the calculations, the activity correction is small compared to the free energy change in the reaction itself.

Table IV shows logarithms of the dissociation

Table III. Types a	of surface reactions	occurring on Fe	-Cr-Al alloys
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A.	Direct oxidation
2C	$Cr(s) + 3/2O_2(g) \rightleftharpoons Cr_2O_3(s)$ , etc.
B.	Solid phase reactions
2A	$l(s) + Cr_2O_3(s) \rightleftharpoons Al_2O_3(s) + 2Cr(s)$ , etc.
C. 1	Formation of spinels
Fe	$O(s) + Al_2O_3(s) \rightleftharpoons FeO \cdot Al_2O_3(s)$ , etc.
D	Formation of silicates
	0 / 1

 $Al_2O_3(s) + SiO_2(s) \rightleftharpoons Al_2O_3 \cdot SiO_2(s)$ , etc.

- E. Decarburization reactions
- $Cr_2O_3(s) + 3C(solid solution) \rightleftharpoons 2Cr(s) + 3CO(g)$ , etc.
- F. Vaporization reactions

 $Cr(s) \rightleftharpoons Cr(g)$ , etc.

Table IV. Dissociation pressures of the oxides

Temp, °C						
	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MnO	CoO
25	85.5	184.6	121.8	144.6	127.2	75.4
200	50.8	112.4	73.4	87.6	77.4	44.5
400	33.0	75.7	48.9	58.8	52.1	28.9
600	23.4	55.8	35.6	43.2	38.4	20.4
800	17.4	43.3	27.3	33.5	29.8	15.1
1000	13.3	34.7	21.6	26.8	24.0	11.4
1200	10.3	28.4	17.4	21.9	19.6	8.8

#### Table V. Solid phase reactions of ferric and chromic oxides with Cr, Al, Si, and Mn

1. 2Cr (s) + Fe<sub>2</sub>O<sub>3</sub> (s)  $\rightleftharpoons$  Cr<sub>2</sub>O<sub>3</sub> (s) + 2Fe (s) 2. 2Al (s, l) + Fe<sub>2</sub>O<sub>3</sub> (s)  $\rightleftharpoons$  Al<sub>2</sub>O<sub>3</sub> (s) + 2Fe (s) 3. 2Al (s, l) + Cr<sub>2</sub>O<sub>3</sub> (s)  $\rightleftharpoons$  Al<sub>2</sub>O<sub>3</sub> (s) + 2Cr (s) 4. 3Mn (s) + Fe<sub>2</sub>O<sub>3</sub> (s)  $\rightleftharpoons$  3MnO (s) + 2Fe (s) 5. 3Si (s) + 2Fe<sub>2</sub>O<sub>3</sub> (s)  $\rightleftharpoons$  3SiO<sub>2</sub> (s) + 4Fe (s)  $= 2Si(s) + 2Cr_2O_3 (s) \rightleftharpoons 2SiO_2 (s) + 4Fe (s)$ 

6.	3S1(S)	+	$2Cr_2O_3$	(s)	₹	35102	(S)	+	4Cr	(S)	

	$\log_{10}K$								
Temp, °C	Reac- tion 1	Reac- tion 2	Reac- tion 3	Reac- tion 4	Reac- tion 5	Reac- tion 6			
25	+54.1	+148.2	+94.1	+62.1	+176.4	+68.3			
200	33.9	92.4	58.5	39.9	110.5	42.6			
400	23.8	63.9	40.1	28.6	77.3	29.8			
600	18.4	48.6	30.2	22.5	59.5	22.8			
800	14.9	38.9	24.0	18.6	48.2	18.5			
1000	12.5	32.2	19.7	16.1	40.5	15.5			
1200	10.8	27.2	16.4	14.0	34.9	13.4			

pressures of the oxides from  $25^{\circ}$  to  $1200^{\circ}$ C as calculated from equations given by Kubaschewski and Evans (19). All of the oxides are stable in the atmospheres and temperatures used in the oxidation experiments.

The equilibrium constants for the several solid phase reactions are given in Table V. All are thermodynamically possible over the temperature range. Although ferric oxide may form initially, both Cr and Al can react to form chromium and aluminum oxide as shown by the positive values of  $\log_{10} K$ . Eventually aluminum oxide should constitute the bulk of the oxide film.

X-ray crystal structure studies (Table II) confirm the thermodynamic predictions that  $Al_zO_s$ should be the chief oxide in the scale. Solid phase reactions may account for the decreases in chromium oxide content of the scale at temperatures above 900°C. The presence of MnO may be due to the high mobility of manganese and to its high thermodynamic stability.

The formation of spinels or other mixed oxide systems may be expected but thermodynamic data for spinels other than Fe<sub>s</sub>O<sub>4</sub> are not available. However, the stability of the several spinels of interest can be deduced from structural information. Table VI shows the lattice parameters of some of the known aluminates (17) having the spinel structure as a function of the ionic radii of the bivalent ions. Table VI shows that Co, Fe, and Mn can form spinels with aluminum

Table VI. Parameters of aluminate spinels of a number of metals

Divalent metal	Atomic number	Radius of ion, A	Parameter of oxide MO,* A	Parameter of aluminate (17) , Å
Ni	28	0.74	4.168	8.06
Mg	12	0.75	4.203	8.10
Co	27	0.78	4.24	8.085
Fe	26	0.80	4.332†	8.119
Zn	30	0.83		8.087
Cu	29			8.09
Mn	25	0.83	4.4345	8.28
Cd	48	0.99	4.689	
Ca	20	1.05	4.797	

\* Coordination number of six.

† Stoichiometric composition.

Table VII. Vapor pressure of metals

remp, °C		$\log_{10}K_p$							
	Fe	Cr	Al	Si	Mn	Co			
400		-23.1	-18.2	-26.3	-14.5	-25.3			
600		-16.1	-12.5	-18.55	-9.6	-17.8			
800		-11.65	-8.95	-13.7	-6.5	-13.05			
900		-9.95	-7.6	-11.8	-5.3	-11.25			
1000	-9.83	-8.55	-6.5	-10.3	-4.35	-9.75			
1100	-8.63	-7.4	-5.5	-8.9	-3.5	-8.5			
1200		-6.4	-4.7	-7.85	-2.8	-7.35			
900 1000 1100 1200	-9.83 -8.63	-9.95 -8.55 -7.4 -6.4	-7.6 -6.5 -5.5 -4.7	-11.8 -10.3 -8.9 -7.85	-5 -4 -3 -2	.3 .35 .5 .8			

oxide. Even though Mn and Co are present in minor amounts in the alloy, they can substitute in the spinel structure and thus appear in the oxide film.

The formation of silicates may be expected from phase diagram studies of the oxides (20). These compounds can exert a major influence on the oxidation process since they may concentrate at the oxide-alloy interface.

The role of the decarburization reaction is not understood. Calculations using data from Kubaschewski and Evans (19) show that, if a carbon content of 0.05% is assumed for the reaction of carbon with ferric oxide, the equilibrium carbon monoxide pressure is 1 atm at 1000°C. Similar calculations for chromic oxide, aluminum oxide, and silicon dioxide show the reaction to occur under vacuum conditions at 1000°C. As the carbon content is depleted, the importance of this reaction diminishes.

Table VII shows the vapor pressures of the metals of interest in this study from  $25^{\circ}$  to  $1200^{\circ}$ C. Except for iron the data are calculated from a recent survey by Stull and Sinke (21). The data for iron are taken from a recent study by the authors (22) using the vacuum microbalance method. The measured values for the vapor pressure of iron were lower than the extrapolated values given by Stull and Sinke (21).

Weight loss calculations based on Table VII for oxide free Fe-Cr-Al alloys show rapid evaporation of Al, Cr, and Mn above 1000°C in high vacuum. However, rapid evaporation of these metals has not been observed in our studies or in other studies (6) on these alloys.

In another study (22) the weight loss curves for oxide free surfaces of pure iron, a 5 Al-Fe alloy and a 5 Al-23 Cr-Fe alloy, were determined. The alloys were prepared from pure metals. The 5 Al-Fe alloy gave a weight loss curve somewhat lower than that for pure iron while the 5 Al-23 Cr-Fe alloy gave a weight loss curve a little higher than that for iron. Chemical analyses of the vaporized deposits showed the vapor from the 5 Al-Fe alloy consisted essentially of iron, while the vapor from the 5 Al-23 Cr-Fe alloy consisted largely of Cr and Fe. We conclude that Al does not vaporize effectively from a 5 Al-Fe alloy. However, Cr and Fe do vaporize from an oxide free surface of a 5 Al-23 Cr-Fe alloy. Other studies (6, 22) show that oxidation of an Fe-Cr-Al alloy reduces the evaporation losses at 1050°C. Since Cr<sub>2</sub>O<sub>8</sub> is not an important component in the oxide scale at 1050 °C, one must conclude that  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> acts as a barrier to the diffusion of chromium.

Table VII shows manganese to have a high vapor pressure. In these alloys manganese is probably combined with sulfur or with oxygen thus lowering its activity, and little manganese would vaporize.

#### Effect of Vapor Pressure in Oxidation

With the exception of oxidation resistant metals and alloy at high temperatures, the vapor pressure of the metal has no direct effect on the mechanism of oxidation. This is because breakdown of normal oxidation processes occurs by other mechanisms, such as loss of adhesion at the oxide-metal interface. The first evidence for a vapor pressure effect was found in the oxidation of chromium (23). The rapid increase in the rate of oxidation of chromium was explained as short circuiting by vaporization of normal ion transfer and diffusion processes. This occurs when the transfer of metal ions into the oxide by evaporation approaches the rate of reaction. Vapor transfer of metal can occur at surfaces other than the metal-oxide interface. In this sense the normal diffusion processes are short circuited. The present study shows a rapid increase in the rate of oxidation at 1050°C for the Fe-Cr-Al alloys. The vapor pressure of the metallic components may be important in the high-temperature oxidation of these alloys, as in the case of chromium.

The vapor pressure effect can be studied in two ways. Compare the rate of evaporation of metal atoms from a free surface with the reaction rate expressed in terms of metal atoms leaving the oxidemetal interface. Since the rate of evaporation has a higher temperature coefficient than the rate of oxidation, a sharp break in the rate of oxidation should occur at the temperature where the two rates intersect. Crystal structure studies also can be used to show the vapor pressure effect. If the volatility of a certain metal becomes important, the oxide of this metal could appear in the oxide film even though other metals form more stable oxides.

Alloy 1 having the lowest rate of oxidation in the 1-2 hr period is the best alloy for checking the vapor pressure effect. Figure 13 shows a plot of the rate of oxidation in terms of both iron and aluminum reacting and the experimental weight loss data for the



Fig. 13. Comparison weight loss 5AI-23Cr-Fe alloy (curve A) with rate of oxidation in terms of Fe (curve B) or AI (curve C), log rate vs. 1/T, alloy 1.

5 Al-23 Cr-Fe alloy. The rate of oxidation shows a sharp break at the temperature where the metal transfer by evaporation equals the rate of reaction.

Table II shows the oxide scale at 1050°C to be  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and a low parameter spinel (probably FeO·Al<sub>2</sub>O<sub>3</sub>). Below 1050°C iron oxides were not observed. Both the rate studies and crystal structure studies show that the high-temperature rate of oxidation and crystal structure of the scale are related closely to the vapor pressure of the metals in the alloy. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale limits in some manner the vapor pressure effect of chromium.

Table II shows for alloy 3, which has the lowest useful life value, the formation of MnO and a trace of  $Cr_2O_a$ . This suggests that the lower aluminum content of the alloy 3 is not limiting the formation of MnO and  $Cr_2O_a$  in the oxide scale.

#### **General** Principles

The selection of metals for high heat resistant alloys based on iron should be made on the following principles: (a) alloying elements should lower the rate of oxidation; (b) solid phase reaction should be considered so as to give an oxide having a good crystal structure match with the metal; this property should maximize adherence of the oxide to the metal and minimize the effects of stress or strain; and (c) alloying elements should be chosen to lower the alloy vapor pressure and to limit the vapor pressure of the more volatile but still desirable elements.

Those studies show that increasing the chromium and aluminum contents in alloys 1 to 3 improves the physical properties of the oxide-metal interface as determined by the strain oxidation experiments. A smaller improvement is noted on the constant temperature oxidation rate.

#### Summary

Three Fe-Cr-Al alloys were studied systematically in regard to their oxidation behavior from 700° to 1100°C. Kinetic studies were made using the vacuum microbalance method. Crystal structure studies were made on the oxide film electrochemically removed from the oxidized alloy. Strain-oxidation studies were made to determine the adherence characteristics of the oxide film. The experimental results were interpreted by thermodynamic and rate analyses of the oxide-metal systems.

Kinetic studies show a unique change in rate of oxidation at 900°C. Over the range of 900°-1050°C the rate of oxidation was nearly constant. Above 1050°C the rate of oxidation again increased. The parabolic rate law could be applied with initial deviations over the complete temperature range. For the temperature range  $700^\circ$ -900°C a logarithmic plot of the parabolic rate law constants vs. 1/T gave a straight line and calculated heats of activation of 76-77 kcal/mole for the three alloys.

Crystal structure studies showed  $\alpha$ -Al<sub>2</sub>O<sub>8</sub> to be the main oxide over the temperature range. Below 950°C some Cr<sub>2</sub>O<sub>8</sub> and MnO were observed. These oxides decreased in the oxide scale on passing through the transition temperature region. At 1050°C the oxide was largely  $\alpha$ -Al<sub>2</sub>O<sub>8</sub>.

The crystal studies confirmed thermodynamic predictions as to the composition of the scale. Solid phase reactions of aluminum with chromium oxide were proposed to explain the shift in oxide composition at 950 °C.

Strain oxidation studies showed the oxide scale on alloy 1 to be less susceptible to damage than the scale on alloys 2 and 3. These studies can be correlated with practical performance tests.

Comparison of the rate of oxidation with available vapor pressure data showed that metal transfer by vaporization was the rate-controlling factor in the oxidation of Fe-Cr-Al alloys at  $1050^{\circ}$ C and above. Design principles were proposed for high heat resistant alloys.

The Fe-Cr-Al alloys are good examples of well designed high heat resistant alloys.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1959 JOURNAL.

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### Deposition of New Chromium-Iron Alloy Plate of Banded Structure

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#### ABSTRACT

A new bath composition and its operating conditions are described for electrodeposition of hard, bright, chromium-iron alloy plate having banded microstructure. A precipitation mechanism is proposed to account for the microstructure of the plate. The process produces plate having almost the same physical properties as conventional hard chromium from a bath composition not based on chromic acid. The plating rate and cathode current efficiency for the alloy are higher than for plating chromium from a conventional bath.

A high-speed chromium-iron-alloy plating process was developed in these laboratories (1). The bath is essentially a chromic- and ferric-alum solution with additions of ammonium sulfate and other salts. In the course of the development program, it was observed that bright chromium-iron-alloy plate having banded microstructure was obtained when hypophosphite was used as a bath additive.

The opportunity to study this particular alloy plate arose when a program for the Navy Department (2) had as its objective the development of hard, wearresistant plate from a high-efficiency bath. Since plates of laminar (banded) structure resemble conventional hard chromium, they were developed with the ultimate objective of improved abrasion resistance.

Preliminary experiments.—Preliminary efforts were successful in depositing bright chromium-iron alloy having banded microstructure onto 2.5-cm (1-in.)-diameter circular areas of steel cathodes
shielded by a 0.8-cm (5/16-in)-deep plastic frame under the following conditions:

# Bath composition (3)

- 700 g/l chrome alum [Cr(NH<sub>4</sub>) (SO<sub>4</sub>)<sub>2</sub> $\cdot$ 12H<sub>2</sub>O] (76 g/l chromium)
- 13.6 g/l ferrous ammonium sulfate [Fe(NH<sub>i</sub>)<sub>2</sub> (SO<sub>i</sub>)<sub>2</sub>·6H<sub>2</sub>O]
- 25 g/l magnesium sulfate (MgSO<sub>4</sub> $\cdot$ 7H<sub>2</sub>O)
- 100 g/l ammonium sulfate [(NH4)2SO4]
- 0.2 g/l sodium dihydrogen phosphate (NaH\_2PO\_{4} \cdot H\_2O)

**Operating conditions** 

Temperature	60°C (140°F)
pH	1.5
Cathode current	
density	54 amp/dm <sup>2</sup> (500 amp/ft <sup>2</sup> )

Lead or chromium-iron alloy anodes were satisfactory for oxidizing and maintaining iron in the ferric state, a condition necessary for the best plating results. The initial oxidation of the iron to the ferric state could also be carried out by the addition of chromic acid to the bath. Apparently phosphate, an oxidation product of hypophosphite, could have been responsible for similar bright, banded plate obtained in earlier work.

# Mechanism for the Deposition of Chromium-Iron Alloy Having Banded Structure

The apparent mechanism responsible for laminar structure of deposits taken from a chromic-ferric sulfate bath containing small amounts of phosphate is that grain refinement and banding result from precipitation of ferric phosphate in the cathode film during electrodeposition. Since confirmation of this mechanism would make development of the bath an easier problem, experiments were designed for this purpose. If the mechanism were correct, silicate, arsenate, and vanadate additions to the bath should have an effect similar to phosphate additions. All these anions form insoluble compounds with ferric iron. Using the conditions for plating with the phosphate additive, the new anions were substituted for phosphate in amounts varying from 0.1 to 1.2 g/l. The results showed the new anions to have the same effect as phosphate with the exception that larger amounts were required (1.2 g/l as opposed to 0.2 g/l).

Actually, the new anions were an improvement over the phosphate additive, because the concentrations required for producing deposits with banded microstructure were not so critical. Slight excess amounts of phosphate caused burning, but this was not true with the other anions. High current density [43-65 amp/dm<sup>2</sup> (400-600 amp/ft<sup>2</sup>)] was required to obtain the desired effects with phosphate and the other anion additives mentioned. The mechanism was supported further by the knowledge that ferric salts of phosphoric, silicic, arsenic, and vanadic acids are insoluble in solutions having pH near 2.7, and that cathode film pH values are higher than bath pH which varied from 0.8 to 2.0 in the tests.

# Development of Bath for Deposition of Plate Having Banded Structure

The precipitation mechanism developed in the preceding section suggested the changes necessary to develop a practical bath composition. A buffer was required to equalize the pH over the entire face of the cathode so that masking of the cathodes with thick frames would not be necessary.

Many amino acids, such as aminoacetic acid (glycine), have isoelectric points in the pH range 2.0 to 2.2 and good buffering capacity in the pH range 1 to 3. They should permit deposition of laminar plate uniformly over broad flat cathodes by maintaining uniformly high pH in the cathode film. Glycine additions, ranging in concentration from 0.5 to 3.0 g/l, were made to the following bath:

450 g/l basic chromic sulfate (76 g/l chromium)<sup>1</sup>

- 13.5 g/l ferrous ammonium sulfate [Fe(NH<sub>4</sub>)<sub>2</sub> (SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] (or 16.6 g/l ferric ammonium sulfate [NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O])
- 20 g/l magnesium sulfate (MgSO4 · 7H2O)
- 100 g/l ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>]
- 1 g/l silicon dioxide (added as water glass, 29.5% SiO<sub>2</sub>)

with the result that uniform deposition of laminar chromium-iron-alloy plate could be achieved on flat rectangular steel panels without any form of shielding under the following conditions:

Temperature	54°C (130°F)				
pH	0.8-1.3				
Cathode current density	21-28 amp/dm <sup>2</sup> (200-260 amp/ft <sup>2</sup> )				
Agitation (work bar)	None to 50 cpm with 3.8 cm (1.5-in.) stroke				
Cathodes	Steel-5 x 15 cm (2 x 6 in.) or 3.8 x 10 cm (1.5 x 4 in.)				
Glycine concentration					
(g/l)	0.5 to 3.0				
Oxidation state	Iron all ferric with little				

<sup>1</sup>Technical grade purchased from Mutual Chemical Company of America.



Fig. 1. Surface crack pattern of banded chromium-iron alloy plate. Note: untouched surface. Magnification 250X before reduction for publication.



Fig. 2. Polished and etched cross section of banded chromium-iron alloy plate. Note: electrolytically etched in dilute oxalic acid. Magnification 500X before reduction for publication.

Data derived from the operation of this bath include the metallographical examination of fourteen deposits to verify the relation between brightness of the deposits and banded microstructure. Uniformly bright plate and complete lack of columnar structure were observed for operating conditions and bath composition cited above. The function of bath constituents was indicated by the following observations:

1. Only mat columnar plate could be obtained if the pH was so low as to solubilize ferric silicate or if the concentration of ferric iron was too low to cause precipitation of ferric silicate at pH 3.

2. Without a buffer (glycine) to equalize pH over the cathode surface, plastic shielding frames and current densities on the order of 53 to 63 amp/dm<sup>2</sup> (500 to 600 amp/ft<sup>\*</sup>) were required for production of uniformly bright and banded plate.

Bath composition was fixed to obtain plate of desired physical characteristics described below. Hence there could be little variation in plate composition from the neighborhood of 85Cr-15Fe. Bath composition was followed by chemical analysis. Iron was maintained by addition of ferrous sulfate or by occasional shifting between soluble Cr-Fe alloy anodes and platinum anodes. The oxidation state of iron was maintained with chromic acid. A few grams per liter of excess chromic acid had no observable effect on the characteristics of the plate. It is noteworthy that no hexavalent chromium had to be present to obtain the alloy plate which resembles hard chromium so long as most of the iron was in the ferric condition.

Bath life and glycine stability were not studied. However, baths were operated 3-4 hr daily for several weeks without any apparent deterioration or need for addition of more glycine.

The procedure according to which the bath was prepared was critical. Solutions of all chromic salts hydrolyze slowly when the temperature is raised. An equilibrium is attained more rapidly when they are cooled from an elevated temperature (over 80°C) to the desired temperature. For this reason a detailed description for bath formulation is given. Bath formulation.—Basic chromic sulfate is added gradually (with constant stirring) to water at  $82^{\circ}$ C ( $180^{\circ}$ F). The initial volume of water is about 60%of the final volume of the bath. When all but a small residue of insoluble matter is dissolved, the ammonium sulfate, ferrous ammonium sulfate, and magnesium sulfate are added with continued stirring. Next, the water glass solution diluted with twice its weight of water is added with vigorous stirring to avoid precipitation of silicic acid.<sup>2</sup>

The solution, still at  $82^{\circ}$ C, is treated with 0.3 g/l activated carbon,<sup>a</sup> usually added as a 4% suspension in water to facilitate wetting. The bath is then aged 4 hr at  $82^{\circ}$ C and 16 hr or longer at near plating temperature. Next, it is filtered at plating temperature, and the pH is adjusted to 1.3 (measured at  $55^{\circ}$ C)<sup>4</sup> with sulfuric acid. The glycine is then added (preferably 1 g/l), and enough chromic acid is added to give a positive external test for hexavalent chromium using S-diphenyl-carbazide indicator.

Typical plate containing 85Cr-15Fe is obtained immediately at  $55^{\circ}$ C, 21 amp/dm<sup>2</sup> (200 amp/ft<sup>2</sup>) cathode and anode current density, using soluble chromium-iron alloy anodes (85Cr-15Fe). The cathode current efficiency is about 35% based on trivalent chromium. Compared with a conventional hexavalent bath with a cathode current efficiency of about 15% (basis Cr<sup>i0</sup>) the trivalent bath with a cathode current efficiency of 35% (basis Cr<sup>i0</sup>) yields about 4.6 times more deposit per unit of electrical current. Such an improvement in electrical efficiency has long been sought in chromium plating. The plating rate is 0.0076 cm/hr (0.003 in./hr) at 230 amp/ft<sup>2</sup> cathode current density.

#### Properties of the Plate

The plate, containing about 85% chromium and 15% iron, has a banded microstructure with a crack pattern (Fig. 1 and 2) similar to that of conventional chromium plate. The as-plated hardness of the plate is 1000 to 1025 Knoop (0.5 kg load) which is about the same as for conventional hard chromium plate. Thin plates up to at least 0.0025 cm (0.001 in.) have the appearance of decorative chromium plate. Thick deposits are still bright, but hazy, because of micro-nodules (see photomicrograph of untouched surface, Fig. 1.) Plates as thick as 0.025 cm (0.010 in.) were mat.

The rate of wear on the Taber Abraser,<sup>5</sup> after a short period of initial wear at 0.65 mg per thousand cycles, is 0.00 to 0.03 mg per thousand cycles. The wear for conventional hard chromium by the same method was 0.00 to 0.01 mg per thousand cycles. The as-plated stress<sup>6</sup> in the deposit is tensile and amounts to 5,000 kg/cm<sup>2</sup> (28,000 psi). This might be termed

 $<sup>^2\,</sup>The\ solubility\ of\ silica\ as\ Si(OH)_4$  is pH independent and is about 0.01% at 25°C and 0.02% at 57°C (4) .

<sup>&</sup>lt;sup>3</sup> Activated carbon, Grade S-51, Darco Department, Atlas Powder Company, New York, New York, was used throughout this work.

 $<sup>^{4}\,\</sup>mathrm{The}\ \mathrm{pH}$  was always measured with a glass electrode standardized at room temperature.

 $<sup>^{\</sup>rm 5}\,\rm Research$  Model E-4010, Taber Instrument Corporation, North Tonawanda, New York.

<sup>&</sup>lt;sup>6</sup> The stress measurements were made with a Brenner-Senderoff Contractometer, Champion Manufacturing Co., New York, N. Y.

residual stress, since stress had been relieved somewhat by cracking.

The frequency of the cracks in the channel-type crack pattern does not appear to vary significantly with bath pH between 1.0 and 1.3, nor with glycine content between 0.5 and 1.5 g/l. Crack counts indicate 250-340 cracks per linear cm (640 to 870 cracks per linear inch) or an average plateau diameter of about 0.0038 cm (0.0015 in.).

#### Conclusions

The results of this research show that a new chromium alloy electroplate containing a minor amount of iron and otherwise having physical properties close to those of conventional hard chromium (a) can be obtained from a bath composition involving little or no chromic acid; (b) derives its characteristic banded microstructure from a precipitation mechanism; (c) can be deposited at a rate of 0.0076 cm/hr (0.003 in./hr) at a cathode current efficiency of near 35% based on trivalent chromium; and (d) can be used as a hard, bright decorative plate. Further study of this interesting bath is required to obtain practical information relative to bath life and to establish a system of soluble and insoluble anodes to maintain bath composition.

# Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1959 JOURNAL.

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# **Electroplating on Certain Transition Metals**

# (Groups IV, V, VI)

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# ABSTRACT

It has been found that transition metals of groups IV, V, and VI can be plated adherently in the as-plated condition by being subjected first to a cathodic treatment which probably covers the surface with a hydride. By this technique, it is possible to eliminate etching prior to plating, permitting better control of dimensional tolerances. If the part is to be heated after plating, the procedure is to deposit a thin film of nickel or iron after the cathodic treatment, vacuum fire, then plate as desired. The method was used to produce adherent coatings of Ni and Cu on Ti, Zr, Nb, Ta, Mo, and W.

A further study was made of Nb and Nb-Ti alloys, in which an anodizing procedure was developed which permits subsequent electroplating of Fe or Ni without requiring etching (thereby permitting close control of dimensions) or annealing treatments (useful where delicate assemblies are involved).

In the past decade, the transition metals of groups IV to VI have become of increasing commercial importance. Accordingly, there has arisen a demand for electrodeposition on these metals. The main reasons for such electrodeposition are: (a) to improve corrosion or high-temperature resistance, and (b) to permit ready joining by soldering, brazing, or welding.

Conventional methods.—The usual method of plating other metals on these elements has involved the following steps: "activation" by etching in a suitable acid, deposition of a thin film of nickel or iron; removal of adsorbed gases; and finally heat treating to improve adhesion of the electrodeposited coating to the substrate. Table I gives recent literature refer-

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ences on the subject; in all cases, a heat treatment is applied after subsequent electrodeposition.

The effect of the etch commonly employed in the methods in Table I is to remove scale, oxide films, and the like, remove skins formed by fabricating techniques, and present a fresh, clean surface for plating. In the case of immersion treatments, the oxidizing agent is hydrogen ion, so that the surfaces also tend to become coated with metal hydride or occluded hydrogen during etching. This is especially true of the group V metals, which are especially prone to hydride formation. For this reason, it is worthy of note that such preplating treatments as cathodic cleaning, commonly employed in preparing many conventional metals for electroplating, have

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Group	Metal	Etch	Method of application	Plating	Ref.
IV	Ti	HF-CH₃COOH	a.c.	Cr	1
		HF-CH <sub>3</sub> COOH	Cathodic or anodic	Cu	1
		SnCl <sub>2</sub>	Immersion	Displacement Cu	2
		HF-HOAc	Immersion: then, a.c.	Cr	37
		HF-HNO-H-SO-	Cathodic: anodic: cathodic	*	38
		FeSO-Al (SO)	camouro, anouro, camouro		
		HF-HBF	Immersion	Ag strike in BF soln.	39
		HF-HCI: HF-HNO.	Immersion	Zn (fluoride-ethylene glycol)	3
		H.POH.SO.	Anodic	Zn (fluoride-ethylene glycol)	3
		$\begin{array}{c} 11_{3}1 \\ 0_{4}-11_{2}50_{4} \\ 101 $	Anodio	Al (other lithium aluminum	1
		AICI3 III ether	Anoule	hydride)	-
		HF-ethylene glycol	Anodic	Cu	5
		HF-CuSO4	Immersion	Cr	6
		$HF-Na_2Cr_2O_7$	Immersion	Cr	6
	$\mathbf{Zr}$	HF-NH₄F	Immersion	Immersion Zn or Ni plating	7, 8
		HF-NH₄F	Immersion	Displacement In	9
	Hf	Little published data. Zr 1	methods should work.		
V	v	Na <sub>2</sub> CO <sub>3</sub> -NaHCO <sub>3</sub>	Anodic	*	10
	Nb	HF	a.c.	Ni; Fe	11, 7
	Та	HF-HC1	Anodic	*	12
		HF-HCl	Anodic	*	13
		HF-H-SO	Anodic	*	14
		NH F-formamide	Anodic	*	15
VI	Мо	KOH-K <sub>3</sub> Fe(CN) <sub>5</sub>	Immersion	Cr (after anodic etch in Cr plating solution)	16, 7
		HCI	Immersion	Cr (after anodic etch in Cr plating solution)	17
		Cu-Zn plating solution	Cathodic	Ni; Fe (after heating to 1000°C to volatilize Zn)	18
		Au strike	Cathodic	Au (after heating to 1400°C)	19
		HF	Immersion	Cr (after anodic etch in Cr	20
		$H_2SO_4$	Anodic	Cr strike, then Ni strike and	21
	w	KOH-K <sub>3</sub> Fe(CN) <sub>6</sub>	Immersion	Cr (after anodic etch in Cr	7
		Cu-Zn plating solution	Cathodic	Ni; Fe (after heating to 1000°C to volatilize Zn)	18
		Au strike	Cathodic	Au (after heating to 1400°C)	19
		HF-HNO	Immersion	*	22
		H.Ooxalic	Immersion	*	23
		H PO_HCIO	Immersion	*	24
		$K F_{\Theta}(CN)$	Immersion	*	25
		1231 C ( C14 ) 6	initial Ston		20

Table I.

\* These references are not directly concerned with plating, but the etches used should be satisfactory prior to plating.

not been mentioned in connection with the substrates of interest in this paper. An exception noted in the tabulation above is the use of strike solutions, which are in effect combined cathodic cleaning and plating solutions.

The principal emphasis found in the literature when electrolytic preplating treatments are employed, is upon anodic treatments, which presumably minimize hydrogen occlusion, or hydride formation. Such treatments, however, are not desirable where accurate dimensional tolerances are involved.

In the course of commercially plating on some of these substrates, a very brief laboratory review was made of typical procedures contained in the table above. In general, it was found that both immersion etch and anodic etch procedures gave reasonably satisfactory results. However, during the course of this limited investigation, intermittent troubles were encountered, usually due to peeling of the as-deposited coating, and also blistering of the coating during the baking step. It was at first thought that these occasional difficulties were due to excessive occlusion of gases, such as hydrogen, on the surface of the substrate prior to plating. Therefore, a preliminary vacuum bake was employed prior to plating. Plating adhesion was found to deteriorate markedly as a result of this operation. This then suggested the possibility that good adhesion was favored by occluded gases, and that perhaps an important function of the preplating etch was to provide such a surface. If true, then it should be possible to substitute for the conventional etch a cathodic treatment in an electrolyte which does not chemically attack the substrate.

It is recognized that impurities often greatly affect the type of results obtained in studies of this type. The substrate used (except for Nb and Nb-Ti alloys) were obtained from A. D. Mackay, and analyzed better than 99.9%; however, no further analyses were made of the impurity contents. The nickel plating solution employed contained the following impurities: Mn, 0.48 g/l; Co, 0.46 g/l; Mg, 0.19 g/l; Fe, 0.028 g/l; Al, 0.018 g/l; Zn, 0.014 g/l; Cu, 0.007 g/l; others, 0.005 g/l. No analysis was made of the nickel electrodeposits on the substrates discussed in this paper. However, nickel deposits on steel made from the same bath as above indicated an impurity analysis consistent with the above figures.

The reagents used for cathodic treatment were A.C.S. reagent grade.

# "Hydride" Plating Procedure

It was indeed found that deliberate evolution of hydrogen on the substrate surface prior to plating markedly improved adhesion of the electrodeposit in the as-plated condition. The essential step in the preplating treatment is cathodic treatment of the metal so as to cause adsorption of hydrogen (with probable formation of surface "hydrides"). This cathodic treatment may be carried out in any electrolyte which does not contain ions of platable metals. Conveniently, dilute mineral acid or alkali metal hydroxide solutions may be used. In this method, the acid etching step may be eliminated, so that no dimensional changes in the substrate occur. However, if the original surface of the substrate is unsound (scale, metallurgically unsound surface skins, etc.) an etch is needed for cleaning purposes.

An example of the procedure is:

1. Soak in alkaline cleaning solution at  $180^{\circ}-200^{\circ}F$ .

2. Rinse.

3. Etch in 10% (wt) HF (see Note 1). Immer-

sion—Ti, Zr, Hf. Anodic at 50 asf—V, Nb, Ta, Mo, W. 4. Rinse.

5. Cathodic for 5-15 sec at 10-100 asf at room temperature in a suitable electrolyte (see Note 2). 6. Rinse.

 Nickel plate for 30 sec to 2 min: NiSO<sub>4</sub>·6H<sub>2</sub>O, 300 g/l; NiCl<sub>2</sub>·6H<sub>2</sub>O, 37.5 g/l; H<sub>3</sub>BO<sub>3</sub>, 37.5 g/l; 65°C; 5-100 asf; pH = 4.

8. Rinse.

9. Plate as desired.

*Note* 1. This step is optional, and is needed only if it is desired to remove the surface and prepare a new, clean one.

Note 2. Suitable electrolytes are 2% (wt) HCl,  $H_2SO_4$ , HNO<sub>3</sub>, HF, KOH, NaOH. The anode should be inert; platinum was used in the laboratory study.

If the part which has been plated is to be subjected to high temperatures during use the hydrogen present under the deposit (in any form) will cause blistering, and lifting of the deposit may result. For such applications, the following procedure is used:

1-8. As above.

9. Dry.

10. Vacuum fire at  $450^{\circ}$ -750°C until gas ceases to be evolved.

11. Nickel strike (Wood's nickel), then plate as desired.

In either of the above procedures, iron plating may be substituted for nickel plating in step 7.

The above procedures were used to obtain adherent deposits (0.2-0.3 mils thick) of Ni and Cu on Ti, Zr, Nb, Ta, Mo, and W. It is concluded that the

procedure would be satisfactory for plating any group IV, V, or transition metal. Adhesion was determined qualitatively only. In the case of wire substrates, conventional bend tests were employed. For rigid substrates, knife or chisel tests were employed. Details of such tests have been given by Ferguson (33). Adhesion was determined on 0.2-0.3 mil deposits only. Undoubtedly, lower adhesion values would be obtained with thicker coatings. However, within the range of coating thicknesses which was explored, the above method gave results equal to or better than those obtained using conventional etching treatments.

# Hydrides on the Surface

The above procedure has been referred to as a "hydride" plating process. The reason for this was to distinguish this procedure from use of conventional cathodic cleaning, as for example, in the preparation of zinc base die castings for electrodeposition, or in the activation of stainless steels prior to plating. In these cases, the saturation of the surface with hydrogen, *per se*, is not the object of the treatment. For the transition metals under discussion, such cathodic treatments have apparently been largely avoided in the past, because of the known ease with which these metals form hydrides. By contrast, this method employed here deliberately saturates the surface with hydrogen.

The word hydride was put in quotation marks in the preceding section because, unfortunately, the very limited scope of the work did not permit proper examination of the cathodically treated surfaces to verify the manner in which the hydrogen was present. However, general reviews on metal hydrides (34, 35) suggest that the hydrides of interest in this paper are so-called "metallic" hydrides. Such materials possess a metallic structure and have metal alloy-like characteristics, lacking stoichiometric formulas characteristic of true electron bonding [for example, Moeller (35) cites ZrH1.92, TaH0.76, VH<sub>0.76</sub>]. X-ray determinations show the lattice of the substrate metals to be distorted, suggesting that the diffusion of hydrogen is interstitial in nature, resembling formation of a metallic solid solution. The hydrogen probably is present in the atomic state, in view of the strong reducing properties of such hydrides. There is evidence that transition metals of group IV, and to a lesser extent, those of group V, form semimetallic hydrides, i.e., hydrides in which evidence of chemical bonding is stronger, and stoichiometric formulas can be obtained. A hypothesis concerning the role of such semimetallic hydrides in plating is presented below.

In any event, all the transition metals are characterized by a tendency to absorb, occlude, or chemically bond with enormous amounts of hydrogen (palladium, for example, taking up 1000 of its volume of hydrogen when treated cathodically). With reference to the procedures discussed in this paper, Hüttig (36) found that Ta takes up about 0.8 H/Ta at room temperature, this figure falling to a very low value above 700°C, indicating that a true chemical bonding is not present, at least at elevated temperatures. Transition metals of group VIII (Fe, Co, Ni) have high permeabilities at elevated temperatures, but absorb little hydrogen reversibly at elevated temperatures. Thus, Hüttig (36) cites an absorption of 0.0004 H/Ni, Fe, or less at 700°C. Thus, in the procedures outlined in this paper, the heat treatment after plating would serve to remove hydrogen from the substrate without adversely effecting the plated deposit. When hydrides of the metals discussed above are removed by heating in a vacuum, decomposition is virtually complete at 800°C (27, 32).

No investigation was made of why it is desirable to have a surface covered with hydride prior to plating (if, indeed, such is the case). Possibly, lattice structure is of importance in this connection. Transition metals of groups V and VI are body-centered cubic. Metals of group IV may be hexagonal close packed, but hydrogen tends to stabilize the bodycentered cubic form (the  $\beta$ -form) (26). Niobium and tantalum hydrides, at lower hydrogen levels, show a definite body-centered cubic lattice (27, 28). With higher hydrogen contents, transition metal hydrides of groups IV and V tend to form face-centered cubic or face-centered tetragonal structures (29-31). Since nickel is usually deposited in a facecentered cubic lattice, it can be seen why the presence of a hydride of similar structure would augment adhesion since electrodeposits adhere best when deposited in the same lattice form as that of the substrate.

# Electroplating on Niobium and Niobium-Titanium Alloys

In the course of the laboratory investigation cited above, particular attention was paid to the problem of plating on niobium and a 75% Nb-25% Ti alloy. The procedure given above was found satisfactory. Equally satisfactory is an etch method suggested by Faust and Beach (7):

- 1. Etch in HF (49% wt) with a.c. at 200 asf.
- 2. Rinse.

3. Dip in 50% (vol) HNO<sub>3</sub> (s.g. 1.43) and 2% (vol) HF (49% wt) to desmut.

4. Rinse.

- 5. Plate with Ni or Fe.
- 6. Bake at 400°F for 22 hr.

7. Heat treat at 1300°F for 1 hr to insure good diffusion bonding.

However, this method is not ideal when close dimensional tolerances are to be maintained. The "hydride" plating procedure would get around this problem, but involves heat treatments just as does the method of Faust and Beach. Accordingly, further work was done to determine whether a method could be developed which would avoid both etching and annealing treatments, for cases where close dimensional tolerances must be maintained and where the nature of the assembly does not permit annealing. Following the type of procedure used successfully with metals such as aluminum, a brief investigation was made of the feasibility of anodizing the substrate as a basis for electrodeposits. Such a procedure would remove no readily detectable amount of metal, require no activation step, eliminate smutting, and obviate the need for subsequent annealing operations to remove occluded hydrogen and/or hydride.

The procedure when using the anodizing method is:

1. Soak in alkaline cleaning solution at 90°C for 2 min. Any strong ferrous electrocleaner may be employed satisfactorily.

2. Rinse.

3. Anodic in 10% (wt) NaOH solution at about 5 v at room temperature to produce yellow (straw) colored film on the substrate. (Any metal not attacked by NaOH may be used as cathode.)

4. Rinse.

5. Coat with nickel or iron: NiCl<sub>2</sub>·6H<sub>2</sub>O, 220 g/l; HCl (sp. gr. 1.18), 125 ml/l; 25°C; 30 asf.

When visibly covered with nickel, rinse and plate: NiSO<sub>4</sub>·6H<sub>4</sub>O, 300 g/l; NiCl<sub>2</sub>·6H<sub>4</sub>O, 37.5 g/l; H<sub>3</sub>BO<sub>3</sub>, 37.5 g/l; 65°C; 5-10 asf; pH = 4.

Or, if iron is desired:  $FeSO_4 \cdot 7H_2O_1$  300 g/l;  $FeCl_2 \cdot 4H_2O_1$  40 g/l;  $(NH_4)_2SO_4$ , 15 g/l;  $60^{\circ}C$ ; 10-20 asf; pH = 4.

6. Rinse.

7. Dry.

8. Heat to red heat in air, or in vacuum for about 2 min.

In the anodizing treatment, the color of the anodized film is critical, the other conditions are not. For example, the NaOH may be as dilute as desired, consistent with rendering the solution conductive. It may be as concentrated as desired, up to the limit of solubility. Temperature of the solution may lie anywhere between freezing and boiling. Formation of an improper film may be detected readily by visual means, by observing the color, as follows: (a) colorless—too thin, (b) yellowish-brown—slightly too thick, and (c) blue or purple—much too thick.

In general, increased film thickness is favored by lower temperatures, higher solute concentration, and higher voltage. Therefore, based on the color of film obtained, suitable adjustment of temperature, concentration, and voltage may be made. The NaOH may be replaced by other alkali metal hydroxides, alkaline salts such as alkali metal phosphates, carbonates, and silicates, and by proprietary alkaline cleaning solutions, particularly those designed for cleaning ferrous parts.

It is possible to combine the cleaning and anodizing steps by utilizing PR in the cleaning step:

1. PR treatment in a strong alkaline electrocleaning solution at  $90^{\circ}$ C at about 5 v, with a cycle of 8 sec anodic and 4 sec cathodic, with treatment time of 2 min.

2. As in steps 4-8 above.

No metallographic cross sections were prepared, but careful stripping indicated that the anodized coating remains on the Nb or Nb-Ti after electroplating. This anodizing procedure has been used to electrodeposit Ni and Fe on Nb and on an alloy of 75% Nb and 25% Ti. Heating the deposit to red heat did not cause blistering or peeling of the deposit, and adhesion remained good, (as determined qualitatively) in spite of the absence of a baking step. Thus, the anodizing method has the advantage over the acid etching and cathodic treatment methods of not requiring an annealing step, and has the advantage over the acid etching method of not attacking the substrate appreciably.

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# A Radioisotopic Study of Levelina in Bright Nickel Electroplating Baths

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## ABSTRACT

A radioisotope-containing addition agent has been synthesized and used as a component in a bright and leveling nickel bath. Investigation by autoradiography and counting techniques shows that this agent is deposited preferentially at the high points of an irregular surface, thereby substantiating a part of leveling theory. The radioactive addition agent also is used in an attempt to understand better the mechanism of formation of laminations in this type of nickel deposit.

In the sequence of events which leads to the production of brilliant, chromium plated parts, the chromium must be deposited on a bright and smooth nickel surface. Such a surface may be produced by buffing a matte or a semi-bright nickel deposit. As an alternative, it is possible to deposit directly, from baths containing organic addition agents, a nickel plate which is bright and which also tends to fill in the micro-irregularities of a surface to make it smooth. Any process which eliminates buffing operations is desirable.

The recognition that certain plating solutions can deposit more than the expected amount of metal in the small recesses or scratches in the basis metal to

produce a smoother surface was reported by Meyer (1) in 1940 and also recognized in the patent literature, prior to the noteworthy contribution of Gardam (1a) in 1947. Although this phenomenon subsequently has been known by a variety of terms, such as "smoothing action" and "hiding power," here it is called "leveling." Leveling has been defined by Thomas (2) as the ability of an electroplating solution to produce deposits relatively thicker in small recesses and relatively thinner on small protrusions with an ultimate decrease in the depth or height of the small surface irregularities. If an irregular surface is considered to be a series of peaks and recesses, then any such action which deposits

more metal in a recess than on a peak contradicts normal plating expectancy. In normal plating, more metal would be deposited on the high current density areas which are the high points, or peaks, of an irregular surface. Thus, in addition to its practical significance, the phenomenon of leveling poses a problem which has enlisted the attention of many investigators, and which has led directly to the study reported here. For a comprehensive review of the whole problem of leveling, the report of Leffler and Leidheiser (3) is most informative.

There has been much speculation concerning the mechanism by which the phenomenon of leveling may occur in the electrodeposition of bright nickel. The situation is complicated by lack of agreement among investigators as to the effect on leveling of various plating conditions, including current density, temperature, agitation, and addition agent concentration (2, 4-7). There is, however, general agreement that an increase in polarization accompanies leveling action (4, 6-12). Some theories of the phenomenon assume that an organic addition agent which promotes leveling is adsorbed or codeposited onto the high points, or peaks, of an irregular surface (2, 4, 7-15). This adsorbed material presumably leads to localized polarization which partially inhibits the deposition of metal at the peaks and diverts current flow to recessed areas. Recent work of Watson and Edwards (7) supports this view. They show conclusively that there is increased polarization in solutions possessing leveling ability. Further, they apparently have identified the presence of addition agents in nickel deposits by a staining technique which, for example, caused a darkening on the peak areas of a deposit obtained from a bath containing thiourea. In his study of laminations, Vanderkooi (15) considered that the dark bands present in deposits contain either included addition agents or their reduction products. These observations point up the need for a technique which will show unambiguously the location of addition agents in leveling nickel deposits.

With the particular solutions used in this study, the deposits formed are laminated in structure. While it is known that leveling can be achieved in unlaminated deposits, a theory which can account at least in part for leveling must be compatible with lamination formation.

The purpose of this study is twofold: to determine if an organic agent known to promote leveling is adsorbed preferentially or codeposited on the high points of an irregular surface, and to develop radiotracer techniques suitable for determining the location, within electrodeposits, of a radioactive organic addition agent.

The work of Vanderkooi (15) has shown that the brightener system sodium allyl sulfonate (16) and N-allyl quinaldinium bromide (17) produces bright, leveling, and laminated nickel deposits. These organic addition agents were used in a Watts type nickel bath to produce the electrodeposits examined in this study. The sodium allyl sulfonate was radioactive due to the use of S-35 in its synthesis.

# Experimental

Synthesis of radioactive sodium allyl sulfonate.— The microsynthesis of sodium allyl sulfonate containing the radioactive isotope S-35 is one reported by Hoekstra (18). The metathesis reaction is carried out between allyl bromide and sodium sulfite containing S-35 as the labeled atom. One-millimole amounts of each of the reactants are heated together in a closed system at 60°C for 35 hr. Excess allyl bromide is extracted by ether using a Soxhlet extractor. The product was dissolved in water to yield a solution concentration such that 1 ml contained approximately 0.003 g of radioactive sodium allyl sulfonate. A radiochemical analysis of the final product showed a recovery of about 95% of the original activity present in the sodium sulfite.

Plating procedure.—The stock nickel solution was a Watts type bath containing nickel sulfate, 300 g/l; nickel chloride, 30 g/l; boric acid, 30 g/l; and a proprietary wetting agent, 5 ml/l. The pH was adjusted to 3.0. Plating was carried out in a small Lucite cell, 2 in. long by 1 in. wide by 3 in. deep. A temperature of 56°-58°C was maintained by immersing the plating cell in a constant temperature water bath. The anode was electrolytic nickel, and agitation was provided by a Hull Cell agitator operating a Lucite paddle which made 110 oscillations per minute. The current density range was from 10 to 55.5 amp/ft<sup>2</sup>, and the plating times varied from 20 to 100 min depending upon the thickness of deposit desired. Due to rapid changes in pH of the small volume of solution used, frequent additions of dilute sulfuric acid were made to maintain a pH range from 2.6 to 3.5.

Inasmuch as a surface consisting of peaks and recesses was desired, grooved cathodes were prepared from brass blocks 1.75 in. by 1 in. by 0.125 in. Grooves 0.030 in. deep, with an included angle of 90°, were cut into one face of the blocks parallel to the long edge. The cathodes had 13 peaks and 12 recesses. To obtain foils of the plated metal, it was necessary to provide a passivated surface. Therefore, the brass cathodes were plated first with a thin deposit of nickel from a sulfamate bath and then passivated by immersion for 1 min in a 0.05% potassium dichromate solution.

The organic addition agent was added to the nickel stock solution in the form of radioactive sodium allyl sulfonate (1 ml equals approximately 0.003 g). Additional nonradioactive sodium allyl sulfonate was added to bring the total concentration up to a range of from 1.5 to 2 g/l. In some of the experiments, a second organic addition agent, N-allyl quinaldinium bromide,<sup>1</sup> was added in sufficient amounts to produce concentrations from 2 to 6 mg/l. All of the additions and plating procedures were carried out under radiochemically safe conditions.

At the conclusion of plating, the cathode was withdrawn from the cell, rinsed with distilled water, and then a scalpel was used to remove the foil from the cathode block. The foil was scrubbed on both top and bottom to remove any adhering material, rinsed with water and with alcohol, and then dried under an infrared lamp preparatory to counting and

<sup>1</sup> Prepared by N. Vanderkooi, Jr., Wayne State University.

Table I. Plating conditions and results

				Brighter concen- tration, mg/ml			
Foil num- ber	Plating time, min	Amp	Current density, asf	No. 1 ac- tive	No. 1 in- active	No. 2 in- active	Result
21	100	0.3	27.3	3	0	0.6	Foil intact, dull
25	100	0.3	27.3	6	0	0.6	Foil intact, dull
26	100	0.2	18.2	6	0	0.6	Foil intact, dull
31	100	0.2	18.2	3	198	0	Foil intact, bright, brittle
34	100	0.2	18.2	3	302	0	Foil intact, dull, brittle
36	100	0.2	18.2	3	198	0.4	Foil intact, dull, very brittle
38	100	0.2	18.2	3	198	0.5	Foil intact, bright, brittle
41	100	0.2	18.2	3	198	0.3	Foil intact, dull. brittle
51	40	0.45	41	3	150	0.2	Foil intact, semi- bright, tough
54	25	0.45	41	3	150	0.2	Foil intact, bright, tough

autoradiography. The data pertinent to the plating conditions and foils produced are presented in Table I. These results are representative of the 65 plating experiments carried out and the 55 nickel foils produced. The foils varied in thickness from 0.0005 to 0.0025 in.

To check whether or not these solutions and conditions produced leveling, portions of cathodes with two different degrees of surface irregularities were plated under conditions identical with those reported above. Duplicate specimens were plated, one in a solution containing only sodium allyl sulfonate, the other in a solution containing both sodium allyl sulfonate and N-allyl quinaldinium bromide. The plated specimens were cross-sectioned, mounted, polished, and etched in 1-1 nitric acid-acetic acid. Fig. 1 shows photomicrographs of a precision reference specimen of surface roughness (2), with a



Fig. 1a. Precision roughness specimen, sodium allyl sulfonate, nitric-acetic etch. Magnification 100X before reduction for publication.



Fig. 1b. Precision roughness specimen, sodium allyl sulfonate nitric-acetic etch. Magnification 500X before reduction for publication.

peak-to-valley height of 0.002 in., plated from a solution containing sodium allyl sulfonate. The original and final roughness measurements made with a topographic microscope showed that leveling did occur. The solution containing both addition agents produced similar leveling.

Counting procedures and autoradiography.-The counting of the plated cathodes and the foils removed from these cathodes was carried out in a proportional flow counter. This procedure provided a gross count of the activity on the top and bottom of the foils but gave no information relative to the distribution of the radioactivity across the surface of the sample. It did, however, give data which were useful in computing autoradiographic exposure times. Several innovations were tried to give more quantitatively useful data which might augment the results of autoradiography. A 0.005-in. thick piece of lead foil was corrugated to duplicate the surface of the nickel foils by pressing the lead into the grooves of one of the cathodes. A single slit, 0.002 in. wide by 1 in. long, was cut in the center of one peak. This piece was then overlayed on a radioactive foil so as to expose only one peak at a time. In this manner, all of the peaks on a foil were counted individually. By turning the lead foil over, it was possible to fit the slit into a valley and count each valley individually. Continuing in this way, a profile of the peak and valley counts was made for both sides of a foil. The results of this method are shown in Table II.

The primary source of information on the distribution of the radioactivity over the surface of a foil has been autoradiography. Since the S-35 gives off a very weak beta ray, it was considered necessary to have the foil in direct contact with the film. Therefore, most of the foils were flattened mechanically, placed between two pieces of film, and then weighted to insure good contact. Past experience has shown that both chemical and pressure effects on the film can result from this method of exposure. In order to insure that everything which appeared on the final autoradiogram was due to radioactivity and not to side effects, foils containing no radioactivity were exposed under identical conditions to check possible chemical interaction and the effects of pressure. These tests showed no influence of side effects. Although several types of film were used,

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### Table II. Lead slit counting data

Fo	oil A	Fo	oil B
Peak	Recess	Peak	Recess
125	94	42	27
115	72	33	33
115	53	76	53
143	63	47	81
213	80	177	91
226	163	163	160
224	212	94	97
125	65	147	34
106	64	43	28
55	55	59	45
79	57	58	

Bottom of Foil\*

Foi	1 A	Fo	il B
Obverse of the peak	Obverse of the recess	Obverse of the peak	Obverse of the recess
248	143	145	58
198	103	133	77
152	133	134	84
120	112	154	65
207	102	135	100
254	113	190	128
227	163	212	126
150	146	176	101
146	129	163	82
181	158	144	80
242	129	102	

\* Counting was done left to right on the top of the foil and right to left on the bottom so that the values in the columns are matched. All values are counts per minute.

the autoradiograms shown in this report were made on Eastman Kodak Type AA film.

Composite data on the counting and autoradiographic exposures are given in Table III, and representative autoradiograms of the top and bottom surfaces are shown in Fig. 2.

The reproductions of the autoradiograms shown in Fig. 2 are positives which are identical with the original autoradiograms. The dark areas indicate the regions of the foils which contain radioactivity. Since it was necessary to make an intermediate negative to achieve this reproduction, some detail has been sacrificed. All of the notches or holes cut into the foils and visible in the autoradiograms were cut so as to identify a peak area. This system of notching not only allowed identification of the individual foils by the number and position of such notches, but also precisely located the peaks and recesses on a given foil.

In addition to visual inspection, densitometric readings on a recording densitometer have been made and are recorded below each autoradiogram in Fig. 2. The apparatus employed was a L&N Linear Recording Densitometer with a General Motors Research Laboratories light source and scanning device. A slit width of 0.005 in. (0.127 mm) was used since narrower ones did not contribute to detail and led to larger instrument fluctuations.



Fig. 2a. Autoradiogram and densitometer trace for the "top" of a foil containing only sodium allyl sulfonate.



Fig. 2b. Autoradiogram and densitometer trace for the "bottom" of a foil containing only sodium allyl sulfonate.

Because this system recorded a marking pip each 0.5 mm, it was possible, by placing a mark near the edge of the autoradiogram, to measure distances from the edge accurately. The instrument was calibrated with a standard step wedge prior to use. Thus, the densities recorded are the actual densities from the exposure to radioactivity when all possible variables in the film processing are kept constant.

As was indicated previously, most of the foils were flattened mechanically to obviate the differences in distance between the peaks and recesses, and the film, during autoradiography. Some of the foils were quite brittle, thereby making this flattening process very difficult. A check was made, therefore, with a representative foil, to determine if the mechanical flattening gave any advantage,

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Table III. Counting data and autoradiography

		Type	Expo- sure		Results	
No.	cpm/cm <sup>2</sup>	film	hr	Image	Detail	ground
21	T-12*	кк	833	Fair	Poor	Heavy
	B-10*	KK	833	Fair	Poor	Heavy
25	T-22	KK	833	Good	Fair	Heavy
	B-30	KK	833	Good	Fair	Heavy
26	T-15	KK	1268	Poor	Poor	Heavy
	B-13	KK	1268	Poor	Poor	Heavy
31	T-1830	K	22	Good	Fair	Heavy
		AA	67	Good	Good	Light
	B-2320	K	22	Good	Good	Heavy
		AA	67	Excellent	$\mathbf{Excellent}$	Light
34	<b>T-850</b>	AA	141	Good	Fair	Light
	B-895	AA	141	Excellent	Good	Light
36	_	AA	66	Good	Good	Light
	B-2231	AA	66	Good	Good	Light
38	T-901	KK	18	Fair	Fair	Heavy
		AA	48	Good	Good	Light
		AA	146	Excellent	Excellent	Light
	B-2116	KK	18	Good	Good	Heavy
		AA	48	Good	Good	Light
		AA	67	Excellent	Excellent	Light
41	<b>T-736</b>	AA	67	Poor	Poor	Light
	B-1656	AA	67	Good	Fair	Light
51	<b>T-585</b>	AA	67	Excellent	Excellent	Light
	B-1434	AA	67	Excellent	Excellent	Light
54	<b>T-804</b>	AA	67	Good	Good	Light
	B-1221	AA	67	Excellent	Excellent	Light

\* T-top of foil; B-bottom of foil. Film processing conditions: temperature, 19°-20°C development time, 4-6 min; developed emulsions on (67°-69°F); both sides of film

either for the autoradiogram or for the subsequent densitometer trace. The foil was formed and then exposed for a given length of time to produce its characteristic autoradiogram. The foil was flattened then and another autoradiogram obtained on the same type of film which was exposed for the same length of time and processed under the same conditions. Visually there were no significant differences noted on the autoradiogram, and the densitometer traces, shown in Fig. 3, indicated that there was no advantage in mechanically flattening these foils.

# **Results and Discussion**

An examination of the autoradiograms shown in Fig. 2 reveals a greater darkening on those portions of the film which were irradiated by the peaks of the foils. In those autoradiograms labeled "top," the difference in density of the lines produced by peaks and recesses is evident, but there is also greater smearing of radioactivity than is apparent on the corresponding "bottom" autoradiograms. The concentration of activity in both instances, however, is much higher on the peaks than in the recesses. This is especially true with the "bottom" autoradiograms which show that the activity is concentrated on the obverse of the "top" peaks. This differential darkening of the films means that there is greater radioactivity emanating from the peaks than from the recesses.







Fig. 3b. Densitometer trace of an autoradiogram made from the same foil after it was mechanically flattened.

The slit-counting data for radioactivity on the peaks and in the recesses, recorded in Table II, serve as quantitative confirmation of the results shown visually by the autoradiograms. Likewise, the densitometer traces made from the autoradiograms show quantitatively the results of distribution of radioactivity over the entire surface. The concentration of activity is highest on the peaks of the "top" autoradiograms and on the obverse of the peaks on the "bottom" autoradiograms. These traces also indicate the manner in which radioactivity increases from a minimum at the bottom of a recess to the maximum at a peak.

In explanation of these results, it is apparent that the ratio of radioactive material (sodium allyl sulfonate or a reduction product containing the S-35) to deposited metal is greater on the peaks than in the recesses. Consequently, there is less selfabsorption of the radioactivity by the thinner nickel metal on the peaks and, therefore, a greater darkening of the film occurs. This explanation is consistent with the fact that in leveling less metal is deposited on the peaks and more metal is deposited in the recesses of an irregular surface. In order to initiate the leveling process, the addition agent first must be concentrated preferentially on the peaks. The autoradiograms and the slit-counting data appear to confirm the assumption of a preferential adsorption or codeposition of the addition agent on the peaks. Actually these results, as well as those recorded in the literature, show only that the agent is concentrated at the peak area. The mechanism of this concentrating action has not yet been demonstrated satisfactorily. While some investigators (7, 14) have shown that certain addition agents apparently are deposited with the metal in an unchanged or unreduced state, the work of Hoekstra (18) and Vanderkooi (15) strongly indicates, in the case of sodium allyl sulfonate, that its reduction product, sulfide ion, is present in the electrodeposited nickel metal. The present work, with this same addition agent, shows only that the labeled S-35 atom is located in the deposit as no attempt was made to distinguish between the possible presence of the sulfonate or the sulfide.

With the type of bath employed in this study, the leveling process is accompanied by the formation of laminations (2, 4, 6, 9, 11, 15, 18, 19). Several investigators (6, 15, 18) have speculated that the "dark" bands contain sulfur, probably in the form of sulfide. It has been proposed by Vanderkooi (15) that the "dark" bands are formed by the reaction between nickel and the reduction product of the sodium allyl sulfonate, while the "light" bands are nickel metal. In order to account for the formation of these laminations, as they accompany the leveling process, it is convenient to assume that both phenomena start with a preferential adsorption of the addition agent on the peaks. It would appear, from an inspection of Fig. 1, that the formation of the laminations is some type of cyclic process wherein alternate layers of metal, and the addition agent or its reduction product, are deposited. The start of this cyclic process and the inhibition of metal deposition on the peaks can be explained by an assumption of preferential adsorption of addition agent.

# Summary

A radioactive organic addition agent, sodium allyl sulfonate, containing the beta-emitting S-35 atom, has been synthesized. This addition agent has been used as a component in a bright nickel plating bath to produce leveling nickel deposits. A radiochemical technique has been developed to locate radioactivity in the deposited metal. Autoradiograms and counting data from the nickel foils produced show that the radioactive addition agent, or its reduction products, is preferentially adsorbed or codeposited on the high points of an irregular surface. On the basis of this evidence, confirmation is obtained for a theory which accounts partially for leveling action in the type of bright and leveling nickel solutions considered in this study.

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# Determination of Crystal Orientation by High Intensity Reflectograms

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# ABSTRACT

An instrument based on the light figure technique for optical orientation of Ge and Si is described which fulfills all requirements for a fast precision orientation of single crystals. The dependence of high intensity reflectograms on etching conditions is shown and standard etching specifications are given.

Reflectograms are light figures obtained by the reflection of light from an etched crystal surface. This method has been developed by mineralogists to obtain information on the location of crystallographic planes and zones in crystals. Many investigators (1) contributed to the light figure method. The method was first applied to germanium and silicon by Wynne and Goldberg (2) and Faust (3). More recently Wolff, Clark, and Wilbur (4) showed that reflectograms of Ge and Si turned out to be very clear and distinct in accordance with the low coordination number and the strong directional bonding forces of these materials.

If reflectograms are used for the orientation of monocrystals, they give excellent accuracy, competing with that achieved by the use of Laue's back reflection technique. Crystals can be oriented accurately by means of reflectograms as already shown for Ge and Si by Wolff and co-workers (4) who oriented Ge and Si single crystals using the (111) reflection within 1.5 min of arc.

The purpose of this paper is to report on a practical instrument for routine orientation work. By use of this instrument it is possible to orient a crystal in any direction and then cut along this predetermined direction without removing the crystal from its original mount. The reflectograms produced are very bright, so the instrument can be operated in a well-illuminated room. The accuracy of orientation is limited by the goniometer error to 12 min of arc for the (111), (110), and (100) reflections in Ge and Si.



Fig. 1. Reflectograms of Ge and directional relationship in: a, (111) plane; b, (100) plane; c, (110) plane.

# Instrument and Method

For optical orientation the crystal surface first is ground and then etched in a specified way. A large number of pits of microscopic size thus are created at the surface of the crystal. These pits are bounded by minute facets which are more or less perfect planes. If a beam of light is directed to such a surface, it splits into a number of components after reflection. If the reflected beam is intercepted by a screen, a light pattern or reflectogram is seen. These patterns show the symmetry of the crystal in the direction of the incident light beam. The pattern for the [111] direction thus shows threefold symmetry (Fig. 1a), the pattern for the [100] direction fourfold symmetry (Fig. 1b), and the pattern for the [110] direction twofold symmetry (Fig. 1c).

The instrument (Fig. 2) consists of an optical system A and a goniometer B for mounting the specimen. The sample can be rotated in both the vertical and horizontal plane without changing the crystal surface to screen distance. A third circle attachment C allows a complete rotation about the horizontal axis of the mounted crystal. The optical system A consists of a 30 watt concentrated arc lamp and a f/1.9 Cintar lens of 50 mm focal length. The screen is a steel plate covered with white paper. A convergent beam of light is focused on the screen, thus achieving very bright reflectograms (5). To orient an ingot, it is cemented onto attachment D as shown in Fig. 2 and D is placed in grooves on goniometer B after removing slice attachment C. The goniometer is built strongly enough to be placed on a cutting machine.

Crystal orientation with a precision of  $\pm 0.5^{\circ}$  of arc is easy to achieve without too much concern for the etching technique. For greater accuracy, however, the etching process is critical. The perfection and shape of the pits developed is strongly dependent on composition of etchant, temperature of etchant, and etching time. For instance, the action of the etching medium might be such that only cubic planes are exposed, thus producing in the (111) plane the well known triangular pit, formed by a three sided pyramid; in the (110) plane an indentation which is saddle shaped; and in the (100) plane a square hole with an uneven bottom. Since the surface in the lower part of these pits is uneven, the resulting reflection is diffused. If these diffused



Fig. 2. Instrument for optical orientation: A, optical system; B, goniometer, transferable to cutting machine; C, third circle attachment; D, ingot mounted for orientation and cutting.

reflections are used for orienting crystals, the accuracy will be less than that obtainable with distinct light figures which correspond to etch pits with flat bottom sections parallel to the plane to be oriented.

The following experimental procedure was adopted: the crystal surface to be checked was hand polished on a glass plate using a water slurry of 500 mesh silica and then etched. The etching solutions, the etching time, and etching temperature as used for Ge and Si are given in Table I. It should be noted that these data apply only to fresh etching solutions. Different etching solutions can be used, but of the ones tried, those listed in Table I gave the most intense reflectograms.

The side walls of the pits in all three planes show a terraced arrangement, corresponding to high index or vicinal planes. These side walls are responsible for the reflections adjacent to the distinct (111), (110), and (100) reflections and aid in identifying different reflections, but their degree of perfection is strongly dependent on etching variables (see Fig. 4 in Ref. 4).

Reflectograms can be used for orientation of single crystals and bicrystals, for tilt angle determination in bicrystals, and many other applications. Once the crystal is etched, measurements can be made in ap-

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	Reflection	Composition of etchant	Time, min	Temp, °C
	(100)	1½ P. HF	12	24
		2 P. H <sub>2</sub> O <sub>2</sub>		
	(110)	4 P. H₂O	12	30
Ge				
		1 P. HF		
	(111)	2 P. $H_2O_2$	6	24
		,4 P.H₂O		
	(100)	50% NaOH solution	12	65
Si	(110)	or	12	65
	(111)	50% KOH solution	6	65



Fig. 3. Ge-(111) reflectogram of 10° misorientation



Fig. 4. (a) Tilt angle  $\phi$  determination in a bicrystal by means of reflectograms. (b) Sketch of a bicrystal showing tilt angle  $\phi$  between the two crystals.

proximately 2 min, a great improvement over the Laue back reflection method.

Figure 3 shows a (111) reflectogram of a Ge crystal which is approximately  $10^{\circ}$  off orientation. The angle of deviation is given by  $\alpha$  and  $\beta$  and is measured by turning the goniometer circles until the center reflection coincides with a predetermined point on the screen obtained for zero settings of the goniometer from a mounted mirror. The horizontal and vertical scale readings of the goniometer then give the amount of misorientation.

An example of tilt angle determination in a bicrystal is represented in Fig. 4a. This picture shows a reflectogram of a bicrystal taken in such a way that the light beam was straddling the grain boundary. The bicrystal is tilted around the [001] direction as shown schematically in Fig. 4b, therefore the reflectogram is taken in the (001) plane which is common to both crystals. Two superimposed (001) patterns show up. The tilt angle is the rotation angle  $\phi$  which can be measured easily.

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# Water-Stabilized Arc Tests on Nonmetallic Materials

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# ABSTRACT

Evaluation of erosion rates on possible high-temperature resistant materials have been carried out in a water-stabilized arc. General classes of materials tested include: graphites and impregnated graphites; ceramics, principally oxides; plastic-ceramic composites; and reinforced ceramics. Results on erosion rates as a function of power dissipated in the arc and time are given, and a general ranking of these materials for high-temperature use is discussed.

Components to function at ultra-high temperatures for short periods range from liners for uncooled rocket engines, where the heat is generated internally, to leading surfaces of high-speed airplanes and missiles which are subject to large heat fluxes as the result of aerodynamic heating, to the experimental machines used in thermo-nuclear research. Temperatures may range up to thousands of degrees; the time of exposure ranges from fractions of a second to minutes.

In order to select or develop materials from which such components can be made, samples of the materials must be tested in an environment comparable to that to which they will be exposed in service. It is desirable that the test duplicate not only the high temperature, but also structural loading, thermal shock, and attack by the gaseous environment to be imposed on the component. One device which has been found useful for the rapid and economical evaluation of materials for resistance to high-temperature gas flow is the fluid-stabilized electric arc.

An arc operating in the vortex formed by a rapidly swirling body of water has developed extremely high temperatures (1). This is due to the increased current density arising from the restricted crosssectional area of the vortex and the cooling of the outer arc regions, which forces most of the current to flow in the center. Peters (2) described an arc in which the cathode consisted of a plate with a hole from which a stream of "plasma" is issued.

The arc used in the present work is struck in a vortex of water between a  $\frac{1}{2}$ -in. diameter graphite rod as anode, and a graphite cathode which is in the

form of a disk with a 3/16-in. hole in the center. The cathode is mounted in a water-cooled horizontal metal plate, which is at ground potential, while the anode is held by a collet in a vertical position directly below the hole in the cathode. Figure 1 is a schematic diagram of the water-stabilized arc. A Lucite "swirl chamber" surrounds the anode. During operation, water is introduced tangentially into this chamber at 36 psi and forms the vortex in which the arc burns.

The power supply consists of four welding generators connected in series. It has been found desirable for stable operation to dissipate about one half the power in a ballast resistor connected in series with the arc, since when the arc is first struck the voltage and current tend to fluctuate. The sample is



Fig. 1. Schematic diagram of water-stabilized arc

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not introduced into the testing position until stable operation has been obtained. Arc voltage is maintained at 180 v by means of a voltage-sensing device connected across the arc and controlling a hydraulic mechanism which feeds the lower electrode at the proper rate to maintain this voltage. The current under these conditions is 350 amp, giving a power dissipation at the arc of 63 kw.

The samples are ½-in. diameter rods 3 or 4 in. long. Usually flat ended samples are used, but in some cases hemispherical ends have been provided: the hemispherical shape is generally lost rapidly. The sample is introduced so that its axis is aligned with the axis of the arc and its end is one inch above the hole in the cathode. An exposure time of ten seconds is usual and an automatic timer records the exact duration of exposure.

With such a facility it is possible to compare various materials for resistance to high temperature. Samples are weighed and their length measured before and after test. Results may be expressed as rate of loss in milligrams per kilowatt second and as loss of length. Such comparisons appear to be valid as long as exposure conditions are held constant.

It would of course be very desirable to define exactly the conditions to which the samples are exposed, but to date such exact definition has not been possible. Temperature, velocity, and composition of the plasma jet should be different at different locations within the jet.

Work has begun to measure conditions within the jet and some preliminary estimates are available. Temperatures have been estimated from  $7,000^{\circ}$  to  $12,000^{\circ}$ K, and velocities from 100 to 1000 m/sec. The composition at the center of the jet has been estimated to be as follows: 10% vaporized carbon; 5% carbon particles from the electrodes; 25% water vapor; 50% dissociated water vapor; 10% ionized atoms and molecules.

In spite of this uncertainty, the arc, used with constant operating conditions, is an excellent tool



Fig. 2. Heat transfer to calorimeter. Nozzle exit, 1-in. diameter.

for preliminary screening and comparison of various materials. However, one useful parameter which may be measured with some accuracy is the rate of heat transfer to a body placed in the jet some distance from the cathode opening. By the use of both solid metal and water-cooled metal calorimeters, it has been possible to establish heat transfer rates averaged radially at various distances from the cathode. Typical results, using a graphite nozzle as a cathode to expand the jet, are shown in Fig. 2.

Not only is it important to determine which materials are most suitable for component fabrication, but also why. A high decomposition temperature and high specific heat are undoubtedly an advantage. An endothermic decomposition would also be favorable. Samples with low thermal conductivity appear to have an advantage; this is doubly useful since the interior of a component made of such material would remain at a relatively low temperature and better retain its mechanical properties during the service life of the component. An additional advantage of materials with low thermal conductivity is that the surface reaches an extremely high temperature, and heat flux due to radiation from the adjacent hot gases is minimized.

Various classes of nonmetallic inorganic materials have been fabricated and tested in the water-stabilized arc. These include: (a) graphites and impregnated graphites, (b) ceramics and reinforced ceramics, (c) ceramic-and-plastic composites.

It should be borne in mind that the ranking given these materials is based simply on erosion rates exhibited in the arc and with a high heat influx-short time application in mind. The ranking for a different environment (lower temperatures, longer times) may be very different.

# **Graphite and Impregnated Graphites**

Graphite has many desirable high-temperature properties which makes it a likely structural material: its refractoriness, low density, low thermal expansion, high-temperature strength, availability of the raw material, machinability, etc. Unfortunately, the oxidation resistance, erosion resistance, and mechanical strength at intermediate temperatures may be too low to permit immediate utilization of any present graphite as a high-temperature structural material particularly in large pieces.

According to current theories, the permeable macrostructure which permits oxygen to penetrate the interior of the material and its microstructure, which is highly reactive to oxygen-containing gases at high temperatures, explains the low oxidation resistance of graphite. The use of pitch binders which partially volatilize during baking and graphitization results in a highly permeable macrostructure, while crystallization into a lamellar structure with weak binding between planes explains the ability of oxygen to break the interplanar bonds which results in low erosion resistance.

Attempts to overcome the undesirable effects of oxidation and erosion include experiments on densification, metal oxide and carbide coatings, and impregnation, chiefly liquid metal and liquid glass im-

Table I. Typical results of water-stabilized arc test on graphites

Material	Grain size*	Impregnant	Length erosion in 10 sec, cm	Weight erosion, mg/kw sec	Final structural state of graphite compared to start
Graphite Z2 (1)	F	None	0.15	0.84	Same
extruded			0.13	0.97	Same
Graphite Z2 (1)	F	None	0.21	0.69	Same
extruded			0.22	0.79	Same
Graphite Z3 (1)	F	None	0.25	0.72	Same
molded			0.23	0.70	
Graphite Z21 (2)	С	None	0.28	0.83	Same
			0.23	0.90	
Graphite Z22 (2)	M	None	0.23	0.65	
			0.20		Same
Carbon Z23 (2)	С	None		End spalled	
Graphite (5)	F	None	0.13	1.10	Same
			0.23	0.61	
Graphite 1 (7)			0.20	0.67	Same
			0.20	0.62	
Graphite 4 (8)		Ves	0.25	0.81	Same
Gruphite I (0)		100	0.20	0.87	

\* F, fine; M, medium; C, coarse.

pregnation of porous graphite. This last approach seems to be the most promising and the most likely to improve the high temperature oxidation and erosion resistance of graphite.

Above 1500°C, graphite becomes stronger mechanically in contrast to most nongraphitic materials; below this temperature, its mechanical strength is about 1/10 that of metals. Its thermal shock resistance is excellent compared to most ceramics but poor compared to metals. It shows practically no ductility below 2200°C, which means there is no relief of localized or unequal stress internally. However, recent work at the Jet Propulsion Laboratory has shown some ductility above 2200°C.

### Graphite Materials System

Graphite materials systems can be divided into at least three types: (a) graphite structures filled with impregnant: the pores in the massive graphite being filled with an impregnant; (b) inorganic or organic structures filled with graphite powder; for example, a cast block of concrete having some of the same replaced by graphite powder; (c) an all-refractory system: a system in which all the ingredients are as equally refractory as graphite. An example would be titanium carbide; here the ingredients could all be added before the mass is graphitized.

Results of water-stabilized arc testing of graphites from many commercial sources showed a very small spread in erosion rates, the average value of which was 1.1 mg/kw sec. The average length loss was 0.25 cm, somewhat higher for more porous graphites.

The best impregnated graphites were found to be a series of composition consisting of silicon carbide and graphite, or silicon metal and graphite which converts to SiC on firing. These show a weight erosion of about 0.6 mg/kw sec and a length loss equivalent to the pure graphite. Since no other impregnant gave better results than pure graphite, the superiority of the carbide-bonded graphite systems seems established, although nitride and boride bonded systems are still to be tested. Other impregnants tested include: oxalic acid, epoxy resin, aluminum sulfate, sulfur, iodine, boric acid, and many others.

Typical test results for graphites and impregnated graphites are given in Tables I and II.

# **Ceramics and Reinforced Ceramics**

Ceramic materials, in general, have poor thermal shock resistance because of their relatively high coefficients of thermal expansion and brittle characteristics. For this reason, most ceramic bodies are not suitable for applications where severe temperature gradients exist. However, successful attempts have been made to increase thermal shock resistance greatly by reducing considerably the thermal expansion coefficients. Unfortunately, the low-expansion ceramic materials are not very refractory. Another approach for improving thermal shock resistance has been to use refractory bodies which are relatively soft and similar to plaster of paris in texture. These materials, when exposed to sudden temperature changes, fail locally at the exposed surfaces while still retaining their strength.

The results of the arc tests on simple ceramics, mostly oxides, are given in Table III.

All samples were obtained from commercial suppliers and were given no further treatment. The fused MgO samples were in the form of  $2 \times 2$ -in. plates varying from  $\frac{1}{4}$  to 1 in. in thickness. Since the plasma jet covered only a  $\frac{1}{2}$  in. circle in the center of the MgO plates, this undoubtedly contributed to the severe thermal shock observed.

A series of ceramic aggregates (listed in Table IV) reinforced by a cementing agent were tested; these unfired cemented bodies had previously exhibited excellent thermal shock resistance when subjected to the exhaust of a rocket motor. Several samples were made from castable mixes containing water, calcium-aluminate cement, or phosphoric acid, and aggregates of bubble alumina and zirconia, magnesia, several grades of commercial alumina grain, and silicon carbide. These samples were tested in the water arc, and the results are shown along with those of other materials in Table IV.

# Table II. Typical results of water-stabilized arc tests on impregnated graphites

Material	Grain size†	Impregnant	Length erosion in 10 sec, cm	Weight erosion, mg/kw sec	Final structural state of graphite compared to star
Silicon carbide			0.51	0.51	
and graphite			0.51	0.54	Same
0-1	F	None	0.25	0.73	Same
Graphite (5)	-	rione	0.23	0.75	Samo
Graphite (5)	я	Repitch treated and	. 0.20	1.64	Same
arapinte (0)	-	regraphitized	0.10	1.04	Same
		Coppor	0.10	2.30	
Graphita (5)		Copper	0.03	0.49	a
Graphite (5)		Calin	0.03	0.47	Same
a 111 (5)		Sodium	0.08	0.96	-20
Graphite (5)	_	Borate	0.15	0.81	Same
	F	Some initial oxidation	0.30	1.94	
Graphite (5)			0.28	1.56	Same
Graphite Al	С	None	0.25	0.86	Same
			Average	1.55	
Graphite Al	С	Sod. sulfate	0.13	1.88	Same or
		Na.SO. 3%	0.18	1.85	better
Graphite Bl	F	None	0.23	0.90	better
drupinte Di	-	Home	0.20	Average	Somo
			0.20	riverage	Same
Craphite Pl	T	Call and a line has	0.20	4.09	
Graphite Bi	r	drogen phosphate hydrated	0.13	4.02 3.91	Same
Porous graphite	М	None	1.02, 0.88, 1.02*	1.96, 1.73	Same as porous graph-
Porous graphite	м	Boric acid	2.28	1.56	Slightly weaker than
I oroup Bruphino		5%	2.28	2.66	porous graphito
Porous graphite	м	Frown rosin	0.51	13.7	Much wookon
I orous graphic	IVI		1 10	15.7	Much weaker
Donous graphito	1.6	04%	0.76	10.7	Come o con concerna a la
Forous graphite	141	36%	1.10	11.5	ite; piece in very
Porous graphite	м	Polyoster	0.38		"Waterburn" and
I bious graphic	IVI	Polyester	0.50		waterburn and
Densus graphito	34	35%	0.76	11.5	Samaaaaa
Porous graphite	IVL	basic crystal 39%	0.70	11.5	ite
Porous graphite	M	Aluminum sulfate hydrated 30%	1.27	10.9 7.2	Much weaker
Porous graphite	м	Sulfur	0.51	14.2	Same as porous graph-
- or our Prubutte	111	47 %	0.76	20.8	ite
Porous graphito	м	Inding	0.76	30.4	Same as porous graph
r orous graphille	TAT	59 <i>%</i>	0.10	34.7	ite

† F, fine; M, medium; C, coarse.
\* Surface temperature by optical pyrometer 2450°C.

The various samples made of  $Al_2O_3$  and MgO eroded quite rapidly compared to the SiC aggregates. Therefore, it appears that the aggregate-type rather than bond-type is more important with regard to erosion resistance. The results indicate that there are no significant differences between samples having different aggregate-size distributions, water content, density, and methods of preparation (casting, troweling, or tamping).

# **Ceramic-and-Plastic Composites**

Although compositions containing organic plastics are not ordinarily considered as refractory materials, certain ceramic-plastic compositions show a surprisingly low erosion rate in the water-stabilized arc tests.

At 3000°C, the organic plastic decomposes into gas and residual carbon as coke on the surface. When glass is present, it fuses and forms a thin viscous layer on the surface which reduces the heat transfer to the model and protects it from the chemical action of the hot gases.

In the 8000°C plasma, even the glass is volatilized, so no liquid protective layer is formed. Here the erosion rate depends on the heat absorbed in converting plastic and glass to vapor at some high temperature and, in the case of supersonic flow, the reduction in heat transfer associated with the addition of the gas to the boundary layer. Since the atoms of the organic part are lighter than those of the glass, the volume of gas generated from a gram of the allorganic material is substantially higher than that from the glass-reinforced material.

Results of arc testing are given in Table V and relative erosion rates for ceramic plastic composites at different temperatures are given in Table VI. Table III. Water-stabilized arc tests on simple ceramics

Material	Wt. loss, g/sec	Wt. loss, mg kw-1 sec-1	Average wt. loss, mg kw <sup>-1</sup> sec <sup>-1</sup>	e Length loss, cm	Comments
Silica-bonded SiC	0.103 0.098 0.103	1.64 1.55 1.64	1.61	0.38 0.33 0.13	
Fused MgO	0.054 0.119 0.139	0.86 1.89 2.21	1.65	0.23 0.28 0.36	Severe ther- mal shock
Fused quartz (SiO₂)	0.139 0.128	2.11 2.03	2.07	0.71	White opaque SiO2 at cold end
SiC (self-bonded)	0.402	6.40	6.40		White coating of SiO <sub>2</sub>
Al <sub>2</sub> O <sub>3</sub>	0.508 0.365	8.06 5.65	6.86	1.04 0.86	
Fused mullite	0.524 0.531 0.449	8.32 8.43 7.92	8.22	1.68 1.65 1.62	
Glass-bonded mica	0.918 0.511	14.6 8.12	11.4	3.82 2.06	Glassy sur- face after test
$\mathrm{ZrO}_2$	0.778 0.735 0.943	12.35 11.65 14.95	12.98	1.40 1.58 1.86	

addie iv. water-stadilized arc tests on reinforced ceram	Table IV.	Water-stabilized	arc tests or	reinforced	ceramics
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Principal aggregate	Bond type	Wt. loss, g/sec	Aver- age wt. loss, mg kw <sup>-1</sup> sec-	Length loss, <sup>1</sup> cm
Al <sub>2</sub> O <sub>3</sub>	Phosphoric acid	_	7.00	_
$Al_2O_3$	Phosphoric acid		8.40	1.42
$Al_2O_3$	Phosphoric acid	0.540	7.80	0.98
Bubble Al <sub>2</sub> O <sub>3</sub>	Phosphoric acid	_	7.30	
$Al_2O_3$	Phosphoric acid	0.576	7.56	0.88
$Al_2O_3$	Phosphoric acid	0.608	9.65	1.68
$Al_2O_3$	Phosphoric acid		7.20	0.86
Fused Al <sub>2</sub> O <sub>3</sub>	Phosphoric acid		7.50	
Fused Al <sub>2</sub> O <sub>3</sub>	Phosphoric acid	0.538	8.58	1.47
Fused Al <sub>2</sub> O <sub>3</sub>	Phosphoric acid	0.515	8.15	1.42
Bubble Al <sub>2</sub> O <sub>3</sub>	Calcium alumi- nate	—	6.80	-
$Al_2O_3$	Calcium alumi- nate	0.559	8.86	1.40
Fused Al <sub>2</sub> O <sub>3</sub>	Calcium alumi- nate	0.635	10.07	1.65
Fused MgO	Calcium alumi- nate	_	7.00	—
Fused MgO	Calcium alumi- nate	0.435	6.90	1.24
SiC	Calcium alumi- nate	0.161	2.57	0.56
Fused mullite	Calcium alumi- nate	0.484	7.65	0.96
Bubble $ZrO_2$	Calcium alumi- nate	0.646	10.25	1.85

Table V. Behavior of various materials exposed to the water-stabilized arc (½-in. diameter rods)

	Weight loss mg/kw-sec
Chopped glass cloth-high temp. phenolic B	6.0
Chopped glass cloth-high temp. phenolic D,	
27% resin	2.7
Chopped glass cloth-high temp. phenolic D, 37% resin	2.2
Chopped glass cloth-high temp. phenolic D, 44% resin	2.2
Chopped glass cloth-high temp. phenolic D, 65% resin	1.5
Chopped refrasil cloth-high temp. phenolic D, 41% resin	2.3
Chopped nylon cloth-high temp, phenolic D.	2.10
57% resin	1.1

Table VI. Relative erosion rates of various materials vs. temperature of exposure

	Ter	nperature	°C
Material	1800	2500	7000
Phenolic-glass cloth, 27% resin	1.0	2.7	2.5
Phenolic-glass cloth, 37%	1.2	2.5	2.0
Phenolic-glass cloth, 44% resin	1.6	2.2	2.0
Phenolic-glass cloth, 65% resin	1.7	1.5	1.4
Phenolic-glass cloth, 41% resin	1.4	1.0	2.1
Phenolic-nylon cloth, 57% resin	4.7	2.5	1.0

# Conclusions

1. A small water-stabilized arc, as described herein, is a suitable device for screening materials considered for short time service at extremely high temperatures. A large number of samples may be tested rapidly and at relatively low cost.

2. The results listed below have been obtained under the conditions described. Only the better plastics and ceramics are included; for example, some ceramics spalled badly and are omitted from consideration.

Materials	Loss of length (When exposed for 10 sec in the plasma 1 in, from the cathode)
Graphite	0.04 to 0.16
Graphite (impregnated)	0.04 to 0.13
Reinforced plastics	0.12 to 0.47
Ceramics	0.13 to 0.40
Copper*	1.0

\* Copper is shown here for comparison only.

3. Extrapolation of these results to other thermal and chemical environments or longer periods of time should not be attempted.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1959 JOURNAL.

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# An Investigation of the Compound Silicon Boride (SiB<sub>a</sub>)

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# ABSTRACT

Single crystals of the compound silicon hexaboride have been prepared. Laue, rotation, and Weissenberg photographs indicate an orthorhombic cell with lattice parameters a =  $14.39 \pm 0.01$ , b =  $18.27 \pm 0.01$ , and c =  $9.88 \pm 0.01$ Å. The pycnometer density is 2.43 g/cm<sup>3</sup>. The average electrical resistivity of single crystals, based on a probe technique, is 0.2 ohm-cm. The melting point is 1950°C. SiB<sub>6</sub> has a Knoop hardness, with a 100-g load, of 1910 kg/mm<sup>2</sup>.

The interest in hard and refractory materials has been prevalent from times dating back to Moissan at the turn of the century. Among the most elusive of these refractory compounds have been the borides of silicon.

Moissan and Stock (1) reported in their original work that they had prepared, by fusion of the elements, two borides, SiB<sub>a</sub> and SiB<sub>a</sub>. The SiB<sub>a</sub> was obtained as black rhombic plates with a density of 2.52 g/cm<sup>3</sup>, and the SiB<sub>a</sub> as black irregular crystals with a density of 2.47 g/cm<sup>3</sup>. The borides were reported to be hard, to have high melting points, and to conduct electricity.

These properties interested other researchers (2-5) who were unsuccessful in their attempts to duplicate the original work. Recently, Samsonov and Latysheva (6) have reported the properties of a tetragonal SiB<sub>a</sub> phase prepared by hot-pressing the elements. Their results and interpretations were questioned by Ormont (7) who found discrepancies in their x-ray data. Samsonov and Latysheva also prepared a compound, SiB<sub>a</sub>, which was studied by Zhuravlev (8) who reported a structure isomorphous with CaB<sub>a</sub>.

Concurrent with the Russian research, a study of the silicon-boron system was underway in our laboratories. A preliminary report (9) has been issued on the formation of the compound  $SiB_{e}$ .

#### Experimental

Preparation.—A review of the methods of preparation of refractory borides and silicides indicated that the synthesis by a combination of the elements was the most logical place to start. The initial experiments were carried out by hot-pressing boron and silicon in a 1 to 3 weight ratio to a temperature of 1700°C. The hot-pressing was performed by induction heating of a graphite mold, which had a boron nitride liner and plungers, using a pressure of 2000 psi and an argon atmosphere. This technique permitted a minimum amount of carbon contamination. Spectrographic analyses of the boron and silicon are given in Table I. The x-ray identification of material obtained by the hot-pressing was difficult due to the presence in the system of unreacted boron which has a complex powder pattern.

To overcome this problem, synthesis experiments were carried out by fusion of the elements at a tem-

perature of approximately 2250°C in an atmosphere of argon. The hold time at 2250°C was usually 1 hr. Fusion was carried out in a boron nitride crucible with a boron nitride lid. The crucible was placed in a graphite susceptor and heated by induction. Fusion experiments were carried out using weight ratios of silicon to boron ranging from 2:1 to 3:1. This was done so that sufficient silicon would be available to react with all of the boron, since a chemical separation of the boron from silicon boride would be extremely difficult. The fused mass was removed from the boron nitride crucible and acid-treated with a mixture of HF and HNO<sub>3</sub> to remove the last traces of free silicon. The crystals were then fused with KOH to remove boron nitride which had formed on the surface. A photomicrograph of a typical melt is shown in Fig. 1. A picture of the crystals after treatment is shown in Fig. 2. After treatment of the melt, the SiB<sub>6</sub> crystals are black and opaque, even when crushed to a fine particle size.

 Table I. Spectroscopic analysis of silicon metal from Electro

 Metallurgical Co.
 (-30 +80 mesh, high purity, acid treated with HCl)

	%
Fe	0.01
Al	0.01
В	0.003
Ca	0.005
Mn	0.0005
Mg	0.0002
(95-97%	) amorphous boron
	%
Fe	%
Fe Al	% 0.7 0.01
Fe Al Mn	% 0.7 0.01 0.1
Fe Al Mn Si	% 0.7 0.01 0.1 1.0 (approx.)
Fe Al Mn Si Cu	% 0.7 0.01 0.1 1.0 (approx.) 0.01
Fe Al Mn Si Cu Cr	% 0.7 0.01 0.1 1.0 (approx.) 0.01 0.008
Fe Al Mn Si Cu Cr Ca	% 0.7 0.01 0.1 1.0 (approx.) 0.01 0.008 0.02
Fe Al Mn Si Cu Cr Ca Mg	% 0.7 0.01 0.1 1.0 (approx.) 0.01 0.008 0.02 0.7

\* Pacific Coast Borax Co., 100 Park Ave., New York 17, N. Y.



Fig. 1. Typical silicon-boron melt. Magnification 6X



Fig. 2. SiB<sub>8</sub> crystals after acid treatment. Magnification 6X

Structure.—A single crystal obtained by the fusion technique shown in Fig. 3 was examined using Laue, rotation, and Weissenberg techniques. The results indicated that the system was orthorhombic with unit cell dimensions of a = 14.39, b = 18.27, and c = 9.88Å. The sample was crushed and a powder pattern was run using a Geiger counter diffractometer. The measured interplanar spacings, as well as the relative intensities, are listed in Table II. CuK  $\alpha$  radiation was used in all cases.

The number of molecules per unit cell, Z, was calculated from the pycnometer density of the compound. Using the observed density of 2.43 g/cc, a value of Z = 40.9 was obtained.

Chemical analysis.—The wet chemical analysis of silicon boride was carried out by first crushing the treated crystals down to -97 mesh particle size in a hardened steel mortar. A 0.2-g sample was analyzed for boron by the method of Blumenthal (10). The silicon analysis required a 0.5-g sample and was carried out using the conventional sodium carbonate fusion. The boron was removed by dissolving out the oxide, after the fusion, by acidifying and treating with methyl alcohol. The alcohol-treated mass was then evaporated to remove methyl borate. Percentages of boron and silicon in crystals prepared by the fusion technique average 69.7 and 29.3, respectively. Values are shown in Table III.

The chemical analysis of SiB<sub>8</sub> is quite close to theoretical values of 69.8% boron and 30.2% silicon. In all cases the boron analyses were run in duplicate.

Nitrogen analyses indicated less than 0.2% N<sub>2</sub> present in the crystals. The SiB<sub>6</sub> is not appreciably affected by solutions of the common acids.

Physical properties.—The apparent melting point of SiB<sub>6</sub> was measured in a small graphite resistance furnace and a value of  $1950^{\circ}$ C obtained. The melting point of Pacific Coast Borax "fused" boron was  $2130^{\circ}$ C, as observed in the same furnace.

A schematic drawing of the internal construction of the melting point furnace is shown in Fig. 4. The behavior of the sample is followed visually through a special close-range optical pyrometer equipped with additional filters designed to extend its operating range to 4200°C. Samples were placed inside a hole drilled in a boron nitride rod. The rod was mounted vertically in a graphite pedestal and the graphite heater placed around the sample. Radiation shields were used around the heater to reduce power loss by radiation. Stepless control of power input to the heater was afforded by a Variac-controlled saturable core reactor. Before a run the furnace was evacuated and then filled with argon. The argon was allowed to flow during the run.

The furnace was calibrated by measuring the melting points of  $Al_2O_3$ ,  $ZrO_2$ , and  $HfO_2$ . The melting

Table II. X-ray diffraction data for SiB<sub>6</sub>

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	"d" (Å)	I.	"d"	I.
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11.47	20	2.74	50
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	9.12	10	2.71	60
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7.62	20	2.67	60
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	5.57	10	2.63	40
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4.92	100	2.60	40
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4.62	40	2.56	30
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4.35	70	2.53	30
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.23 (Doublet)	80	2.48	20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.15	50	2.47	20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.99	20	2.40	30
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.86	40	2.36	30
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.70	30	2.34	20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.53	10	2.26	20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.45	30	2.21	20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.39	30	2.15	10
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3.25	40	2.11	10
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3.18	30	2.08	10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.10	20	2.04	20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.05	20	2.01	10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.98	30	1.98	10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.93	30	1.93	10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.85	80		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.89	20		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.85	20		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.83	20		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.82	20		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.77	20		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.71	40		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.67	30		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.62	40		
$\begin{array}{cccccccc} 1.552 & 20 \\ 1.546 & 10 \\ 1.482 & 30 \\ 1.444 & 30 \\ 1.434 & 30 \\ 1.424 & 30 \\ 1.369 & 10 \\ 1.356 & 20 \\ 1.350 & 20 \end{array}$	1.57	20		
1.546     10       1.482     30       1.444     30       1.434     30       1.424     30       1.369     10       1.356     20       1.350     20	1.552	20		
1.482     30       1.444     30       1.434     30       1.424     30       1.369     10       1.356     20       1.350     20	1.546	10		
1.444     30       1.434     30       1.424     30       1.369     10       1.356     20       1.350     20	1.482	30		
1.434     30       1.424     30       1.369     10       1.356     20       1.350     20	1.444	30		
1.424         30           1.369         10           1.356         20           1.350         20	1.434	30		
1,369         10           1,356         20           1,350         20	1.424	30		
1.356 20 1.350 20	1.369	10		
1.350 20	1.356	20		
	1.350	20		



Fig. 3. Single crystal of SiB<sub>6</sub>. Magnification 22X

points agreed with published values within experimental error which was assumed to be  $\pm$  20°. Correction for the glass window in the furnace was made using Wien's law. A more complete description of the apparatus is given by Lambertson and Lewis (11).

The electrical resistivity of crystals of SiB, was determined by a "probe" method (12,13). The resistivity was of the order of 0.2 ohm-cm as compared with 6x10<sup>s</sup> ohm-cm for the resistivity of the boron used. It is not possible from these measurements to conclude a reason for this low resistivity for SiB<sub>6</sub>; however it is consistent with the low resistivity reported for B<sub>4</sub>C (14).

The hardness of SiB, was measured on single crystals which were mounted in black bakelite. Samples of silicon carbide, boron, and boron carbide were mounted in the same mount so that a direct comparison could be made. The mount was first roughpolished on a 100-grit diamond wheel. The final polishing was done with a 400-grit diamond wheel followed by 500-grit SiC waterproof paper with a final finish using diamond dust on a polishing cloth.

The samples were indented using a Leitz Mini-

Sample	Perce	ntage con	Percentage silicon
1*	76	.53	23.02
2†	69.	.05	29.43
3†	70.	.30	28.92
4+	70.	.16	29.48
5†	69.	.4	29.3
	Theoretical	Composition	
	Boron	69.8	
	Silicon	30.2	

Table III. Chemical analysis of SiB.

\* Hot pressed slug (had free boron),  $\uparrow$  Single crystals by fusion of elements. Note: Percentages were obtained after treatment of the melt with HF + HNOs to remove free silicon followed by fusion with KOH to removed boron nitride. Nitrogen was analyzed to be less than 0.2%.



Fig. 4. Schematic drawing of melting point furnace

load Durimet Tester. The indenter was the Knoop diamond point and the load 100 g in all cases. The hardness values are listed in Table IV.

#### **Discussion of Results**

The difficulties experienced by previous investigators in preparing single crystals of SiB<sub>6</sub>, as evidenced by the literature survey, appear to have been the result of several factors, of which the most pertinent are:

1. In most instances the reaction was carried out at too low a temperature. It appears that it is necessary to be above the melting point of boron, which is approximately 2130°C.

2. Reactions generally were carried out in the presence of carbon, which appears detrimental to the reaction since silicon and boron tend to form their respective carbides. The fact that a crucible material such as boron nitride was available was indeed fortunate, since silicon carbide and graphite had proven unsatisfactory.

3. A slow cooling rate is essential particularly since indirect evidence indicates that a peritectic reaction is involved.

4. A sufficient amount of silicon is necessary to react with all of the boron, as the final separation of SiB<sub>6</sub> from boron or other compounds is extremely difficult. With this in mind it appears that a two to one weight ratio of silicon to boron is satisfactory.

Structure-Cell dimensions were determined from rotation and Weissenberg photographs.

The orthorhombic structure reported here for SiB<sub>6</sub> is not in agreement with the CaB<sub>6</sub> structure reported by Zhuravlev. X-ray data reported by Zhuravlev matches that for CaB<sub>6</sub>, but since no chemical analysis is reported it is not possible to conclude that the pattern applies to SiB<sub>6</sub>. The solution to the complete structure should prove interesting since a similarity to B<sub>4</sub>C (15, 16) is indicated.

Table IV. Knoop hardness measurements

	L*	Range $HK_{100}$	Avg. HK <sub>100</sub>
Boron	24.3	1940-2630	2410
B <sub>4</sub> C	21.6	2910-3160	3050
SiC	23.6	2510-2580	2560
SiB	27.3	1740-2050	1910
		14230. P	

 $HK_{100} = Knoop hardness = \mathbf{L}^2$ 

where P = load grams, L = length of indentation in microns

\* Values for L are an average of 10 indentations.

The chemistry of the borides indicates that one might well expect various other borides of silicon, but as yet no evidence for the SiB, phase reported by Moissan has been found.

Physical properties.-The density as determined by the pycnometer method is quite reproducible. The value of 2.43 g/cm<sup>3</sup> is slightly less than the 2.47 g/cm<sup>3</sup> quoted by Moissan. The density for SiB<sub>3</sub> (2.43 - 2.49 g/cm<sup>3</sup>) as determined by Samsonov indicates a compound similar to SiB. The density of the SiB, prepared by Samsonov was reported by Zhuravlev to be 2.16 g/cm<sup>3</sup>.

The observed melting point for SiB, is approximately 1950°C, which is about 200°C below that of elemental boron.

The breakdown of SiB, upon melting as observed by x-ray studies suggests a peritectic reaction, but further work will be necessary before the various phases of the binary diagram are established.

The measured hardness of SiB<sub>6</sub> is lower than anticipated from the reported hardness of silicon borides. In view of the hardness values reported by Samsonov it is felt that there may be other silicon borides that will give the expected hardness. SiBe is not as prone to cracking under loading as boron or boron carbide.

#### Summary

1. Single crystals of silicon boride (SiB<sub>6</sub>) have been prepared and identified by wet chemical and x-ray analyses.

2. SiB<sub>6</sub> has an orthorhombic structure with unit cell dimensions of a = 14.39, b = 18.27, and c = 9.88Â.

3. SiB<sub>6</sub> has a density of 2.43 g/cm<sup>3</sup> based on pycnometer measurements.

4. The number of molecules per unit cell based

on a density of 2.43 g/cm<sup>3</sup> is 40.9.

5. The melting point of SiB<sub>6</sub> is approximately 1950°C.

6. The electrical resistivity is approximately 0.2 ohm-cm based on probe measurements of single crystals.

7. The Knoop hardness of SiB, is approximately 1910 kg/mm<sup>2</sup> using a 100-g load.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1959 JOURNAL.

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# The Electrolytic Preparation of p-Methoxyphenylacetonitrile

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#### ABSTRACT

Conditions necessary for the electrolytic preparation of p-methoxyphenylacetonitrile from  $\alpha$ -hydroxy-p-methoxyphenylacetonitrile and its esters were determined polarographically. Polarographic reduction waves were obtained in dioxane and water only in the presence of tetrabutylammonium iodide and tetramethylammonium iodide. Alpha-benzoxy-p-methoxyphenylacetonitrile which was reduced at the most positive potential gave no reduction wave in the presence of either ammonium chloride or lithium chloride.

On the basis of the ease of reduction and ease of preparation  $\alpha$ -benzoxyp-methoxyphenylacetonitrile was used as the starting material in the large scale reduction at a mercury cathode and gave p-methoxyphenylacetonitrile in yields averaging 65%.

The preparation of *p*-methoxyphenylacetonitrile is of interest since this compound is an intermediate in the synthesis of numerous alkaloids and synthetic drugs (1, 2). The chemical methods reported are numerous and have involved the metathetical reaction of anisyl chloride with alkali cyanides, the nitration of phenylacetonitrile followed by reduction, diazotization, hydrolysis, and methylation, the catalytic reduction of  $\alpha$ -benzoxy-p-methoxyphenylacetonitrile, and the reaction of acetic anhydride with the oxime of p-methoxyphenylpyruvic acid (3).

The present study describes the electrolytic preparation of p-methoxyphenylacetonitrile from a-benzoxy-p-methoxyphenylacetonitrile. Polarographic data were used to determine the conditions necessary for the electrolysis and the derivative of  $\alpha$ -hydroxy-p-methoxyphenylacetonitrile most suitable for this preparation.

### Experimental

The esters of  $\alpha$ -hydroxy-p-methoxyphenylacetonitrile and  $\alpha$ -hydroxyphenylacetonitrile (mandelonitrile) were studied polarographically in solutions having the following compositions: (A) 0.175M tetrabutylammonium iodide and 0.0048% methyl red in 75% dioxane; (B) 0.175M tetrabutylammonium iodide in 75% dioxane; (C) 0.0972M tetramethylammonium iodide in 47% dioxane; and (D) 0.1312M tetramethylammonium iodide in 50% dioxane.

The current voltage curves were obtained with a Fisher Elecdropode having a current scale calibration of  $0.0196\mu a/unit$  on the galvanometer scale at a sensitivity of one and a Sargent Model XII polarograph having a current scale calibration of 0.00497  $\mu a/mm$  at a sensitivity of one.

All measurements were made in a water thermostat at  $25^{\circ} \pm 0.1^{\circ}$  using both a cell with a mercury pool as an anode and a H-type cell fitted with a saturated calomel electrode. The potential of the mercury pool was measured in the various solutions against a saturated calomel electrode (S.C.E.) using a sintered glass salt bridge of the type described by Laitinen (4).

The dropping mercury electrode had the following characteristics. At a pressure of 70 cm of mercury the drop time in 0.1N KCl was 4.3 sec. (open circuit). The value of m was 1.58 mg sec<sup>-1</sup> with a calculated value of  $m^{2/3}t^{1/6}$  of 1.73 mg<sup>2/3</sup> sec<sup>-1/2</sup>.

Materials.—The dioxane was purified by refluxing with metallic sodium until the molten sodium remained shiny. This process usually required about a week. The ammonium chloride, lithium chloride, and tetramethylammonium iodide used were of a reagent grade. Tetrabutylammonium iodide (5),  $\alpha$ -benzoxyphenylacetonitrile (6),  $\alpha$ -ethoxycarbonyloxyphenylacetonitrile (6),  $\alpha$ -hydroxy-p-methoxyphenylacetonitrile (6), α-ethoxycarbonyloxy-pmethoxyphenylacetonitrile (7), a-benzoxy-p-methoxyphenylacetonitrile (6), and  $\alpha$ -acetoxy-p-methoxyphenylacetonitrile (8) were made according to the directions given in the literature.

Electrolysis .- The reduction was carried out in a circular battery jar, 15.7 cm in diameter and surrounded by an ice bath. A 5 x 13 cm porous cup, which was 4-mm thick, was used as the anode compartment and was supported by a small Lucite stand 3 cm above the surface of the mercury pool used as the cathode. The cathode had an area of 193.8 cm<sup>2</sup> and was connected to the external circuit by a glass tube filled with mercury and with a small platinum wire sealed in one end. The anode was a large platinum gauze electrode. An efficient mechanical stirrer was mounted in the cathode compartment close to the surface of the mercury pool.

The anode and cathode compartments were filled with 1700 ml of 0.1M tetramethylammonium iodide in 50% dioxane. To the cathode solution  $\alpha$ -benzoxyp-methoxyphenylacetonitrile (20.0 g) was added. The line potential was 80 v. The initial current of 1.7 amp increased to 3.9 amp in the first 20 min as the temperature increased from 21.5° to 50.0°. This current, which corresponded to a current density of 0.020 amp/cm<sup>2</sup>, and the temperature were maintained at this point for an additional hour. Gas evolution occurred after 1 hr of electrolysis. To insure complete reduction the electrolysis was continued for a total of 6 hr during which time the current density dropped to 0.010 amp and the temperature to 30°. During the entire period the cathode solution was kept neutral by the dropwise addition of glacial acetic acid (10.65 ml). The resulting catholyte was treated with 800 ml of water, and the dioxane was removed under reduced pressure as an azeotrope. The resulting solution which contained an oil was then extracted with ether. The ether extract after washing with 5% hydrochloric acid and 5% sodium hydroxide gave 13.75 g of an oil which gave two fractions when distilled under reduced pressure. The first (2.5 g) of these, bp 100°-120° (20 mm) corresponded in boiling point to benzyl alcohol; it was not, however, investigated any further. The second fraction (6.3 g, 57% yield), bp 163.5°-164° (22 mm) consisted of p-methoxyphenylacetonitrile,  $n_p^{17.0} = 1.5392$ . Further proof for the structure was obtained by condensing the product with anisaldehyde in the presence of alkali (9). The product a-(p-methoxyphenyl)-p-methoxycinnamonitrile melted at 107°-109° and did not depress the melting point of an authentic sample (10).

In a smaller run using 10 g of  $\alpha$ -benzoxy-pmethoxyphenylacetonitrile 4 g of p-methoxyphenylacetonitrile was obtained (72.5% yield).

### Results

The polarographic data obtained for the various substituted phenylacetonitriles are given in Table I.

All the the compounds except  $\alpha$ -hydroxy-p-methoxyphenylacetonitrile gave well-defined waves. The latter gave a drawn out wave.

Alpha - benzoxy - p - methoxyphenylacetonitrile failed to give a polarographic wave in either 0.1Mammonium chloride or 0.1M lithium chloride in 75% dioxane.

The large-scale electrolytic reduction of a-benzoxy-p-methoxyphenylacetonitrile in 50% dioxane containing 0.1M tetramethylammonium iodide gave

Table I. Half-wave potentials and diffusion currrent constants for various substituted phenylacetonitriles

Compound -phenylacetonitrile	Concn. millimoles liter	Solu- tion*	$E_{1/2}(v)$ S.C.E.	Ia†
α-Benzoxy	1.00	Α	-1.65	2.86
α-Ethoxycarbonyloxy	1.00	D	-2.12	3.62
a-Hydroxy-p-methoxy	1.00	в	-1.72	1.73
a-Acetoxy-p-methoxy	1.05	в	-2.02	1.92
a-Benzoxy-p-methoxy	1.00	Α	-1.65	2.06
a-Benzoxy-p-methoxy	0.055	С	-1.73	1.60
α-Ethoxycarbonyloxy- p-methoxy	1.01	в	-2.07	5.17

\* For the composition see the Experimental section.  $\uparrow I_d = i_d/Cm^{2/3} t^{1/6}$ .

in two runs p-methoxyphenylacetonitrile in yields amounting to 57 and 72.5%, respectively.

### **Discussion of Results**

An examination of the results in Table I indicates that the  $\alpha$ -benzoxy derivatives of the two phenylacetonitriles are reduced more easily than the other esters. This behavior points to a greater tendency for the phenyl groups in comparison with the ethoxy and methyl groups to withdraw electrons from the ester linkage and thus make this bond more susceptible to reduction. A similar effect is found in the corresponding analogous acids; benzoic acid is more acidic than acetic acid. No value is reported for the dissociation of ethyl bicarbonate, but this acid would be expected to have approximately the same acidity as carbonic acid since the inductive effect of the ethoxy group approximates that of the hydroxyl grouping.

The diffusion current constant obtained for these benzoates pointed to the following electrode reaction.

$$p-CH_sOC_sH_sCHCN + 2e + H_sO \rightarrow$$
  
 $OCOC_sH_s$   
 $p-CH_sOC_sH_cH_sCHC^- + OH^-$ 

This process was confirmed by the formation of *p*-methoxyphenylacetonitrile in a large-scale reduction. No benzoic acid was isolated in this reduction since the potential was not controlled. A fraction boiling at approximately the same point as benzyl alcohol was obtained, however, and may be formed from the benzoate ion since this is reducible at more negative potentials.

Alpha-hydroxy-p-methoxyphenylacetonitrile and  $\alpha$ -acetoxy-p-methoxyphenylacetonitrile from their diffusion current constants undergo a similar reduction to p-methoxyphenylacetonitrile and hydroxide and acetate ions, respectively. The lower values obtained for the currents may be caused by decomposition of these compounds in solution.

The higher diffusion coefficient constants obtained for the  $\alpha$ -ethoxycarbonyloxy derivatives suggests that possibly four electrons are involved in the reduction of these compounds. The reduction of these esters to the phenylacetonitrile would involve two electrons and produce the ethyl carbonate ion. This ion can hydrolyze at the dropping mercury electrode to carbon dioxide and ethanol. Carbon dioxide has been shown to undergo reduction at the dropping mercury electrode to formic acid (11) and would be the basis for the higher current observed. The overall electrode reaction for the reduction of the  $\alpha$ -ethoxycarbonyloxy derivatives would be the following:

On the basis of the ease of reduction and the ease of preparation  $\alpha$ -benzoxy-p-methoxyphenylacetonitrile was used as the starting material for the large-scale electrolytic preparation of p-methoxyphenylacetonitrile. Tetramethylammonium iodide was used as the supporting electrolyte because it was less expensive than the tetrabutylammonium iodide. The average yield of 65% obtained indicated that the electrolytic method offered a suitable way for the preparation of p-methoxyphenylacetonitrile.

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# The Electrochemistry of Nickel

# I. Codeposition of Nickel and Hydrogen from Simple Aqueous Solutions

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# ABSTRACT

The simultaneous electrodeposition of nickel and hydrogen has been studied in chloride and sulfate solutions and the individual polarization curves determined from efficiency measurements. Nickel polarization has a Tafel slope of 0.10 and is independent of pH and type of anion at constant nickel ion activity. The nickel polarization data can be explained readily in terms of the transfer of a nickel ion from the solution across an unsymmetrical potential energy barrier to the metal phase. The hydrogen overvoltage evaluated during codeposition at constant pH is substantially the same for both chloride and sulfate solutions with a Tafel slope of 0.12. Hydrogen and nickel deposition appear to occur without any appreciable interdependence over the range of conditions involved in the present work.

The electrodeposition of nickel has been studied by various workers in the terms of polarization measurements (1-8), structural studies (9-13), and efficiency measurements (7, 14). With only a few exceptions, these measurements have been made in nickel solutions containing two or more anions in appreciable concentrations and often various addition agents. Experimental results obtained with such relatively complicated systems are not conducive to fundamental interpretation.

The present investigation has been directed to the determination of the various parameters associated with the electrodeposition of nickel from relatively simple aqueous solutions containing only one type of anion at a time in any appreciable concentration, i.e., sulfate or chloride. The cathodic polarization and current efficiency with respect to nickel deposition have been measured in sulfate and in chloride solutions as a function of nickel ion concentration, pH, and temperature. From these data, the activation polarization for both nickel deposition and hydrogen deposition has been calculated (15) as a function of current density for each process.

Reiser and Fischer (7) have reported on the simultaneous deposition of hydrogen and nickel from a nickel chloride-hydrochloric acid solution and have calculated the individual polarization curves according to the procedure mentioned above. These authors then compared the nickel polarization curve from the simultaneous discharge with the corresponding curve for the deposition of nickel from a boric acid buffered, nickel chloride solution for which the efficiency was close to 100%. Hydrogen polarization for the simultaneous discharge was compared with that for a nickel surface in a pure hydrochloric acid solution. The polarization curves for nickel electrodeposited from the two different

<sup>1</sup> Present address: National Carbon Research Laboratories, Parma, Ohio. <sup>2</sup> Present address: The Kemet Company, Cleveland, Ohio. solutions were found to be reasonably close in view of the differences in the nickel ion activities and the possibility of nickel hydroxide formation near the cathode at a pH as high as 4.4. Major differences were found for the hydrogen overvoltage curves. On the basis of the latter comparison, Reiser and Fischer concluded that the hydrogen and nickel deposition processes are dependent on each other during codeposition on a nickel surface.

Such comparisons are not without question. For example, in the hydrogen overvoltage comparison, no consideration appears to have been given to the differences in the hydrogen ion activities or salt effects. A specific objective of the present research has been to examine further the interdependence of the polarization curves for nickel and hydrogen during simultaneous discharge in terms of the dependence of these processes on nickel and hydrogen ion activities in both chloride and sulfate solutions.

#### Apparatus

Such factors as mass transport, current distribution, electrochemical purity, and temperature must be controlled carefully in polarization measurements. The polarization cell shown in Fig. 1 has been designed with these factors in mind. The Pyrex cell consists of two U-tubes at right angles to each other with the two U-tubes joined by a T-connection at the cathode compartment. Several small sidearms (not shown) have been incorporated to facilitate the introduction of auxiliary electrodes and a solution bridge to an external reference electrode for pH measurements as well as for the filling and subsequent withdrawal of the solution from the cell. The cathode assembly was introduced through a ground joint at the top of the cell while the anode was introduced through a second ground joint (not shown) in the other end of the U-section containing the cathode. The centrifugal glass stirrer and associated drive system, represented diagrammatically



Fig. 1. Polarization cell

in Fig. 1, were used to circulate the electrolyte past the cathode surface at a controlled rate with the direction of flow as shown by the arrows. The solution within the cell was saturated with purified hydrogen gas, usually by means of a fritted glass disk. Temperature was controlled to  $\pm 0.05$ °C by means of a thermostatic control mounted within the outer bath in Fig. 1.

The majority of the polarization measurements have been made by the direct method. The Luggin capillary was introduced through the rear of the cathode since this arrangement did not interfere with the flow of the solution past the cathode surface. This advantage more than offsets the possible disadvantage associated with slightly nonuniform current density distribution at the electrode surface. Any *IR* drop effects associated with the use of the rear Luggin capillary arrangement were shown to be negligible on the basis of a check made by the interrupter method.

The cathode design is shown in Fig. 2. A metal disk with an area of approximately 1 cm<sup>2</sup> and a thickness of 1/8 in. was mounted in the cured plastic Castolite.<sup>3</sup> A glass capillary tube with an internal diameter of 1/16 in. extended from the inside of the cathode assembly to the outside. The outside end of the glass capillary tube was ground so as to be flush with the surface of the nickel disk. Electrolytic leakage between the inside of the cathode assembly and the nickel through a path around the outside of the glass capillary tube was not a problem since the capillary tube was cast in the plastic.

The reference electrode for the cathodic polarization measurements was a mercury-mercurous chloride, saturated potassium chloride, reference electrode (S.C.E.). Reagent grade chemicals and triply distilled mercury were used in the preparation of the reference electrode. For all measurements, the reference electrode was maintained at the same temperature as the polarization cell. In order to minimize contamination of the solution within the



Fig. 2. Plastic cathode assembly with rear-type Luggin capillary.

cathode compartment, an intermediate solution bridge filled with the same solution as in the cell was used between the solution in the rear of the cathode assembly and the reference electrode. Two asbestos-filled capillaries were placed in this solution bridge to prevent any appreciable convection.

The anode for the polarization measurements in nickel sulfate solutions consisted of a platinum foil in the form of a cylinder. This cylinder was welded to a platinum wire which, in turn, was sealed into a soft glass tube. For the chloride solutions, the platinum anode was not used because of possible difficulties associated with liberation of chlorine within the cell. For the chloride solutions, the anode consisted of a cylinder of nickel with a thick plate of nickel electrodeposited from a Watts bath which had been prepared from reagent grade chemicals. The anode was inserted into the cell through a ringsealed joint. A separate gas vent was incorporated in the anode compartment in order that any gaseous products liberated at the anode would be swept out with the hydrogen, and hence, would not reach the cathode compartment. The anodic efficiency in the chloride solutions with the electroplated nickel anode was close to 100%.

Polarization was measured with a L&N K-1 potentiometer in conjunction with an Eppley unsaturated Weston standard cell. A conventional regulated, filtered powder supply capable of delivering 350 v at 200 ma with a large series resistance was used as a source of polarizing current. The current through the cell was determined by measuring the *IR* drop developed across a standard 10.00-ohm resistance in series with the cell.

The velocity of the electrolytic solution was determined as a function of the voltage output of the electrical tachometer by means of a Pitot tube with an entrance of 1 mm ID. By varying the position of the tip of the Pitot tube in the cathode compartment, it was established that the velocity of the solution was at a maximum at a level corresponding to approximately the top of the intersection in Fig. 1. For this reason, the cathode assembly was placed in the cell in such a way that the cathode surface was

<sup>&</sup>lt;sup>3</sup> Castolite Company, Woodstock, Ill. This plastic is an unsaturated polyester resin and is insoluble in all common solvents when properly cured.

just a slight distance below the top of this intersection. The final velocity vs. tachometer measurements were made with the cathode assembly in the cell.

### Experimental Procedure

The solutions were prepared from recrystallized reagent grade nickel sulfate and chloride. The effect of pre-electrolysis of the electrolytic solutions with platinum electrodes was examined during the preliminary polarization measurements and found to be negligible at potentials for which appreciable nickel electrodeposition occurred. This finding concerning pre-electrolysis is somewhat surprising in view of the general need for pre-electrolysis in polarization studies. The effects of impurities on the polarization. however, are probably considerably less in the case of the deposition of a metal wherein a new surface is constantly being created. At higher pH, the preelectrolysis caused considerable changes in the pH. As a result, pre-electrolysis was not used for the majority of the measurements reported in this paper.

The exact concentration of nickel in the various solutions was determined by the cyanide method (16). The pH of each solution was determined by measuring the potential of a hydrogen electrode in the particular electrolyte vs. an S.C.E. While the precision of these measurements was of the order of 0.01 pH unit, the accuracy was less because of liquid junction potentials. The pH of each solution was adjusted to specific values through the addition of either hydrochloric or sulfuric acid to the electrolyte.

The preparation of the cathode surface was as follows. The nickel cathode was first abraded to yield a fresh surface with medium grade (320 A) silicon carbide, waterproof emery paper, wetted with water, and then polished further with fine waterproof emery paper (400 A) until the surface of the nickel disk appeared uniformly smooth. The electrode surface was subsequently etched for 45 sec in a 5N nitric acid solution. After the surface was thoroughly rinsed with distilled water, the cathode was quickly inserted into the polarization cell and the solution velocity adjusted to approximately 45 cm/sec in the bulk of the solution adjacent to the cathode. The polarizing current was then adjusted to 15 ma/cm<sup>2</sup>, and the electrodeposition of nickel continued at this current density for 10 min. This period of time has been found sufficient for the cathode to attain an essentially steady-state condition with respect to potential.

After 10 min of preplating, the polarization was carefully measured at a current density of exactly 15 ma/cm<sup>3</sup>. The current density was then increased to 55 ma/cm<sup>3</sup> and the potential recorded again as soon as a stable value was attained. This usually required less than 30 sec. Polarization measurements were made subsequently at current densities of 45, 35, 25, 10, 6, 4, 2, 1, 4, and 15 ma/cm<sup>2</sup>. In each case, a second repeat run was made under similar circumstances with a 10-min preplate period. In the second run, polarization measurements were made at the current densities of 15, 50, 40, 30, 20, 15, 12, 8, 5, 3, 1.5, 3, 5, and 15 ma/cm<sup>2</sup>. Area increments under these conditions were negligible. After the completion of the run, the pH of the electrolyte was again checked with the hydrogen electrode. The pHchange during any one run usually was less than 0.02 pH unit.

The cathode efficiencies for the electrodeposition of nickel were determined at the potentials associated with current densities of 55, 40, 25, 15, 8, and 5 ma/cm<sup>2</sup> for each solution composition and temperature involved in the polarization studies. In some cases, the amount of nickel that could be deposited in any reasonable time was so small that conventional weighing operations were not suited to the determination of the amount of nickel electrodeposited. Consequently, the procedure adopted for this purpose involved the anodic dissolution of the deposited nickel in hydrochloric acid solution followed by the analysis of the solution for nickel by the cyanide method (16). The electrolytic cell used for the anodic dissolution is described elsewhere in detail (17). The cathode assemblies used in the efficiency studies were similar in design to those shown in Fig. 2 with the exception that the disk of nickel was replaced with a similar disk of silver. The silver surface was preplated with nickel at a current density of 15 ma/cm<sup>2</sup> for 10 min in much the same fashion as in the case of the polarization measurements. The amount of nickel electrodeposited during the preplate time was carefully determined and subtracted from the total amount of nickel deposited on the cathode in the subsequent measurements.

The structural properties of the electrodeposited nickel were examined by means of x-ray diffraction techniques. A modified Wyllie (18) camera, specifically constructed for the examination of electrodeposits, was used for this work. A North American Phillips x-ray diffraction tube with a cobalt target provided an incident x-ray beam at an angle of approximately 15° relative to the surface of the electrodeposit. A cylindrical projection of the diffracted x-rays was obtained. The depth in the deposit to which the x-ray pattern was sensitive was checked by depositing a known amount of nickel on a silver surface and then examining the diffraction pattern for lines corresponding to silver. In the final x-ray examination, the deposit thickness was adjusted so as to prevent the preplated nickel from registering directly in the x-ray diffraction patterns. Because of the relatively small angle of incidence of the x-ray beam, deposits of only a few ten-thousandths of an inch thickness were generally sufficient.

# **Experimental Results**

Flow rate.—At  $45^{\circ}$ C for all of the solutions involved in the present work, the cathodic polarization was found to approach a limiting value with increasing flow rate even at current densities as high as  $55 \text{ ma/cm}^{a}$ . This was not the case at  $25^{\circ}$ C in the more dilute solutions. Even at the highest available solution velocities (50 cm/sec) in the 0.12M nickel sulfate, the polarization attained a limiting value only at current densities less than  $25 \text{ ma/cm}^{a}$ . For this reason, the majority of the polarization measurements have been made at  $45^{\circ}$ C. Although the



Fig. 3. Comparison of polarization measurements by the direct and interrupter methods. Potentials are negative to the saturated KCI calomel electrode (S.C.E.) at the same temperature. Solution: 0.5M NiCl<sub>2</sub> with a pH of 2.0 at  $25^{\circ}$ C, adjusted by addition of HCI.

polarization attained a limiting value as the solution velocity was increased, it cannot be assumed that the concentration polarization was negligible. The increase of the velocity of flow in the bulk of the solution beyond a certain value probably has relatively little effect on the effective thickness of the diffusion layer at the cathode solution interface. The attainment of a limiting value for the polarization at high flow rates, however, is important because reproducible concentration gradients are then established at the electrode surface. In no case was a limiting current density found with respect to the discharge of either nickel or hydrogen. Unless otherwise indicated, all of the polarization measurements reported in this paper were made with a maximum flow rate in the bulk of the electrolyte adjacent to the cathode surface of 45 cm/sec.

Reproducibility.—In Fig. 3, cathode potentials (negative to an S.C.E. reference) are plotted against total current density for a 0.5M nickel chloride solution with a pH of 2.0 at 25°C. The data noted by the circles were obtained by the procedures described above, whereas the data indicated by the squares were obtained in subsequent measurements by Griffis (19) in a glass polarization cell of somewhat different design. The interrupter method was used for the latter measurements with cathodes of 0.25  $cm^2$  area with purified hydrogen gas bubbled through the solution. The electronic equipment has been described previously (20). In both cases, the



Fig. 4. Dependence of cathode potentials on current density at various temperatures in 0.5M salt solutions of pH 2.0. Potentials negative to S.C.E. at the same temperature; pH adjusted by addition of HCI or  $H_sSO_s$ .



Fig. 5. Dependence of cathode potentials on current density at various pH in 0.5M salt solutions at 45°C.

flow rates in the solution adjacent to the cathode were in excess of 40 cm/sec. The agreement between the two independent sets of measurements is within  $\pm 2$  mv.

Further evidence of the reproducibility in the present work can be found in Fig. 4-6 in terms of the smooth curves which can be drawn through the experimental points despite the fact that two separate runs were involved in obtaining the points for each curve. The agreement between the polarization measured at 15 ma/cm<sup>2</sup> at the start of each run and that measured at the same current density at the end of each run was usually within  $\pm 1$  mv and at the worse  $\pm 3$  mv.

Polarization data.—In Fig. 4-6 are presented typical cathodic polarization data for the simultaneous deposition of nickel and hydrogen from chloride and sulfate solutions for various temperatures, pH, and nickel salt concentrations. The ordinates represent cathode potentials (negative to S.C.E.) and include a small liquid junction potential. Variations in the junction potential with solution composition are believed to be small compared to the changes in the cathode potentials arising directly because of changes in the activities of the hydrogen and nickel ions. Current densities represented in these figures are based on the apparent areas of the cathodes.

Polarization measurements have been limited to apparent current densities of  $10^{-3}$  to  $10^{-1}$  a/cm<sup>2</sup> for the following reasons. At current densities below  $10^{-3}$  a/cm<sup>2</sup>, the predominant process is the discharge of hydrogen and the polarization values become somewhat nonreproducible, probably because of insufficient control of impurities. Under such circumstances, impurity effects are accumulative. At cur-



Fig. 6. Dependence of cathode potentials on current density at various salt concentrations at pH 2.0 and 45°C.



Fig. 7. Dependence of cathode potential on current density for nickel electrodeposition at various salt concentrations at pH 2.0 and 45°C.

rent densities above  $10^{-1}$  a/cm<sup>2</sup>, concentration polarization becomes significant in solutions of relatively low nickel ion concentration and high pH.

Polarization curves for the discharge of nickel at  $45^{\circ}$ C are presented in Fig. 7-9 for various nickel ion concentrations, pH, and temperatures. These curves have been derived from the over-all polarization data and the efficiency data. At least part of the deviation from linearity at higher current densities is associated with concentration polarization, and perhaps all of it.

In Fig. 10-12 are the polarization curves for the discharge of hydrogen at various nickel salt concentrations, pH, and temperatures. As in the case of the nickel polarization curves, deviations from linearity can be explained in terms of concentration polarization. Mass transport problems should be particularly severe at the higher pH as is evident from the curve for pH 2.43 in the 0.5M NiSO, solution in Fig. 11.



Fig. 8. Dependence of cathode potential on current density for nickel electrodeposition at various pH in 0.5M salt solutions at  $45^{\circ}$ C.



Fig. 9. Dependence of cathode potential on current density for nickel electrodeposition at various temperatures in 0.5M nickel chloride at pH 2.0.



Fig. 10. Dependence of cathode potential on current density for hydrogen discharge at various salt concentrations at pH 2.0 and 45°C.

The differential capacity of the nickel cathode was measured by the interrupter method in the 0.50M nickel sulfate solution at a pH of 2.0 and temperature of 45°C. The value was found to be 75  $\pm$  $3 \mu f/cm^2$  of apparent surface area over the complete range of potentials represented in Fig. 4-6. If the value of 28.8 µf/cm<sup>2</sup> of true surface area as determined by Brodd and Hackerman (21) for nickel in 1M Na<sub>2</sub>SO, at 30°C is assumed applicable at potentials negative with respect to the zero point of charge, the roughness factor is approximately 2.5. In Fig. 10. the hydrogen polarization exhibits little variation with the type or concentration of nickel salt. Likewise in Fig. 8, the nickel polarization exhibits only minor dependence on pH particularly in chloride solution. This implies that the roughness factor does not change to any appreciable extent with pH. salt type, or salt concentration. Little question exists as to the constancy of the roughness factor during a



Fig. 11. Dependence of cathode potential on current density for hydrogen discharge at various pH in 0.5M salt solutions at  $45^{\circ}$ C.



Fig. 12. Dependence of cathode potential on current density for hydrogen discharge at various temperatures in 0.5M nickel chloride at pH 2.0.

<b>Table I. Polarization</b>	data	for	hydrogen	discharge	and	nickel	deposition
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				Hy	drogen discharge	•	N	ickel depositi	on
Salt	Molarity	Temp, °C	pH	В	α	$-\log i_0$	В	$\alpha z$	$-\log i_{\theta}$
NiCl <sub>2</sub>	0.50	25	2.00	0.123	0.48	6.6	0.103	0.57	5.4
	0.12	45	2.00	0.130	0.49	5.9	0.103	0.61	5.0
	0.25	45	2.00	0.139	0.45	5.8	0.098	0.64	4.7
	0.50	45	2.00	0.134	0.47	5.9	0.098	0.64	4.5
	0.50	45	1.49	0.120	0.53	6.1	0.093	0.68	4.6
	0.50	45	2.41	(0.143)	(0.44)	(5.6)	0.100	0.63	4.5
NiSO,	0.12	45	2.00	0.117	0.54	6.4	0.105	0.60	5.0
	0.25	45	2.00	0.111	0.57	6.4	0.104	0.61	5.0
	0.50	45	1.49	0.120	0.53	6.1	0.093	0.68	5.0
	0.50	45	2.43	(0.144)	(0.44)	(6.6)	0.091	0.69	5.5

\* Bracketted values are dubious because of concentration polarization with respect to hydrogen ions or because of limited accuracy for the hydrogen discharge current. When the efficiency for nickel deposition is close to 100%, the errors in the hydrogen discharge current become quite significant.

given polarization run in view of the reproducibility of the initial and final polarization values at a total current density of 15 ma/cm<sup>2</sup>.

In Table I are summarized the polarization data for the discharge of hydrogen and nickel ions in terms of the Tafel slopes (B), the logarithms of the exchange current  $i_o$  in a/cm<sup>2</sup> of apparent area, and  $\alpha z$ , where  $\alpha$  is the fraction of the potential effective in changing the energy of activation for the cathodic rate-determining step, and z is the charge of the species passing over the energy barrier. For hydrogen, z = 1, while for nickel, z can be assumed to be equal to 2 if the rate-determining step involves the transfer of a nickel ion from the solution to the metal phase. The coefficient  $\alpha$  is approximately 0.50 for hydrogen discharge with no significant difference in this coefficient between the sulfate and chloride solutions within the limits of experimental error. Likewise, the average value for the coefficient  $\alpha z$ for nickel discharge is 0.65 and does not appear to differ significantly between sulfate and chloride solutions.

The calculation of the values for  $\log i_{o}$  requires a knowledge of the reversible potentials of the hydrogen and nickel electrodes in the particular electrolytic solutions involved in the present work. For hydrogen, this is not a problem since the potentials of the reversible hydrogen electrode in these electrolytic solutions vs. S.C.E. were determined directly as part of the adjustment of the solutions to particular pH values. In the case of nickel, however, the reversible potential vs. the S.C.E. is much more difficult to establish because the reversible potentials could not be measured directly under the present experimental conditions. Furthermore, the best literature values for the standard electrode potential for nickel are probably accurate only to 10 mv. Even with data for the standard electrode potential for nickel, the uncertainties concerning liquid junction potentials and single ion activities interfere with the accurate calculation of the potential difference between the reversible nickel electrode and the S.C.E. In the present work, this potential has been evaluated for both sulfate and chloride solutions on the basis of the following equation:

$$E = -0.470 - (1.0 \cdot 10^{-3}) (t-25) + (0.9915) (10^{-4}) T \log a_{\star}$$
[1]

where  $a_{,}$  is the activity of the nickelous ion and tand T are the temperature on the Centigrade and absolute scales, respectively. This equation is based on the data of Carr and Bonilla (22) for the thermogalvanic potentials of nickel in 0.1 and 1.0M nickel sulfate solutions. In using the above equation for chloride as well as sulfate solutions, the assumption has been made that the liquid junction potentials and the temperature coefficients are the same for the chloride solutions as for the sulfate solutions. This assumption is probably valid to within a few millivolts.

The activities of the nickelous ion have been calculated for the sulfate solutions from the mean activity coefficients evaluated by Harned and Owen (23) from the isopiestic vapor pressure data of Robinson and Jones (24), and for the chloride solutions (25) from the isopiestic vapor pressure measurements of Robinson and Stokes (26). For the nickel sulfate solutions, the activity coefficient of nickelous ion has been assumed equal to the mean activity coefficient. For the chloride solutions, the activity coefficient of the nickelous ion was set equal to the square of the mean activity coefficient on the basis of the Debye limiting law. Furthermore, the values for the activity coefficients at 45°C have been assumed to be the same as at 25°C, an approximation which appears justified in view of the limited accuracy of Eq. [1]. In the case of the nickel sulfate solutions of pH 1.49, the amount of sulfuric acid added in the course of adjusting the pH was appreciable compared to the nickel sulfate concentration (0.5M). This partially was taken into account in the activity coefficient calculations by using the mean activity coefficient of nickel sulfate solutions of the same ionic strength as that of the sulfuric acidnickel sulfate solutions.

The accuracy of the values for the apparent exchange current  $i_o$  is limited more by the accuracy of the value for the Tafel slope than the reversible potential. The uncertainty in the Tafel slope is particularly great for solutions in which either the concentration polarization is appreciable or the current densities for hydrogen discharge are uncertain because only a small fraction of the total current is involved in hydrogen discharge, e.g., hydrogen polarization curve in Fig. 11 for 0.5M nickel chloride at pH 2.41. On the basis of the roughness factor of

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Table II. Orientation and arain size of nickel electrodeposited at 45°C

		Current			
Salt	pH	density, ma/cm <sup>2</sup>	Orientation*	Grain size†	
0.5M NiSO4	1.5	5	R	1	
		15	[100]	2	
		40	[100]W	2	
	2.5	5	R	1	
		15	[100]	2	
		40	[110]	1	
0.5M NiCl <sub>2</sub>	1.5	5	R	2	
		15	[100]	3	
		40	[100]W	3	
	2.5	5	R	2	
		15	R	4	
		40	[100]W	2	

\* Random = R; Weak = W. † Grain size scale: 1 to 4 (increasing size).

2.5, discussed earlier, the quantity -0.4 should be added to log i, values in Table I to obtain the logarithm of the exchange current per unit true area.

X-ray diffraction.—The x-ray diffraction studies indicated that all of the deposits at 45°C from chloride and sulfate solutions have a face-centered cubic lattice. The diffraction patterns show a tendency for two types of preferred orientations as well as small changes in grain size. These results are summarized in Table II on a relative basis. In no case was the tendency for preferred orientation strong. The lack of any preferred orientation at the low current densities is surprising, particularly since the preplate had a small tendency for the [100] plane to be parallel to the surface. At the higher current densities, the [110] plane tends to be parallel to the surface for the sulfate solutions.

The grain size is compared qualitatively on a scale of 1 to 4, where 1 represents the finest grain

Table III. Hydrogen overvoltage data for nickel in hydrochloric and sulfuric acid solutions according to other workers

Electrolyte	Temp, °C	Tafel slope	—log i	• Worker
0.0003M HC1	_*	0.090	6.7	L., L., & F. (30)
0.0012M HC1	—	0.090	6.7	L., L., & F.
0.013M HC1		0.10	6.5	L., L., & F.
0.15M HCl		0.10	6.0	L., L., & F.
0.001M HC1	20	0.093	6.6	B. & P. (29)
0.001M HC1	40	0.104	6.0	B. & P.
0.01M HCl	20	0.091	6.7	B. & P.
0.01M HCl	40	0.094	6.1	B. & P.
0.1M HCl	20	0.104	6.0	B. & P.
0.1M HC1	40	0.106	5.7	B. & P.
1.0M HC1	20	0.109	5.4	B. & P.
1.0M HCl	40	0.120	4.2	B. & P.
$1M \operatorname{NiCl}_2 + 1M \operatorname{HCl}$	20	0.06	9.5	R. & F. (7)
$1M \operatorname{NiCl}_2 + 1M \operatorname{HCl}$	30	0.07	8.3	R. & F.
$1M \operatorname{NiCl}_2 + 1M \operatorname{HCl}$	40	0.07	8.1	R. & F.
$1M \operatorname{NiCl}_2 + 1M \operatorname{HCl}$	50	0.07	8.1	R. & F.
0.1M H <sub>2</sub> SO <sub>4</sub>	25	0.110	6.6	B. & R. (31)
0.01M H <sub>2</sub> SO <sub>4</sub>	25	0.110	6.4	J., Y., & H.(27)
0.05M H <sub>2</sub> SO <sub>4</sub>	25	0.095	6.3	J., Y., & H.
0.5M H <sub>2</sub> SO <sub>4</sub>	25	0.097	4.5	J., Y., & H.
$0.05M H_2SO_4 + 0.45M$	_0			
K <sub>2</sub> SO <sub>4</sub>	25	0.135	6.6	J., Y., & H.

\* No temperatures appear to have been given by Lukovzev, Levina, and Frumkin (30).

and 4 the coarsest for the samples which were examined. This scale is believed to have covered a small range of grain size with the variation in size between the limits of the scale estimated to have been less than 1 to 3. No consistent trend is evident with increasing current density, although the grain size was generally smaller with the nickel sulfate solutions than the nickel chloride solutions.

### Interpretation of Experimental Results

In systems involving simultaneous electrode processes, the assumption is often made that the current densities associated with the individual processes can be calculated on the basis of a constant effective area for each process. In Fig. 7-12 for nickel and hydrogen discharge, the Tafel slopes are substantially constant over a tenfold change in current density in the instances where concentration polarization is not large. This constancy of the Tafel slopes supports the above stated assumption. Likewise, the hydrogen discharge appears to be independent of nickel deposition on the basis of the linearity in the Tafel plots for hydrogen as well as the minor and probably negligible effect which variations in nickel salt concentration appear to have on the hydrogen polarization curves (see Fig. 10).

The values for the derivative of the cathode potential with respect to pH at constant hydrogen discharge current, evaluated near the middle of the linear ranges in Fig. 11, are 0.11 and 0.10 for hydrogen discharge<sup>4</sup> from sulfate solutions and from chloride solutions, respectively, provided the curve for pH 2.41 in 0.5M nickel chloride is not considered. These values compare favorably with the value of  $2.3RT/\alpha F$  predicted (28) for the dependence of the electrode potential on pH when hydrogen is deposited in acid solution in the presence of a neutral salt for the case where either the hydrogen ion discharge step or the electrochemical desorption step is ratedetermining. This relatively close agreement however, is to be expected only in the absence of specific ionic adsorption.

Unfortunately, hydrogen overvoltage data are not generally available in the literature for purposes of comparison with the present data since it is necessary to duplicate both pH and ionic strength. Table III summarizes hydrogen overvoltage data of Bockris and Potter (29) and of Lukovzev, Levina, and Frumkin (30) for room temperatures. Values for the 0.01 and 0.013N hydrochloric acid solutions in Table III differ by small, although significant amounts from the Tafel slope of 0.123 and the log  $i_a$  value of -6.6listed in Table I for the 0.5M nickel chloride solution of pH 2.0 at 25°C. Such differences might be anticipated in view of the large concentration of salt present during the codeposition of hydrogen with nickel as well as the dependence of the Tafel slope on the pretreatment of the nickel surface (27).

The Tafel slopes and log  $i_o$ , calculated from the graphs published by Reiser and Fischer (7), also have been listed in Table III. These values are based

 $<sup>^4</sup>$  Values for  $-\log i_{\theta}$  in Table I are far too limited in accuracy to permit the effects of varying pH on the kinetics to be examined in terms of the apparent exchange current density.

on polarization measurements obtained during the simultaneous deposition of hydrogen and nickel. They differ from those obtained by other workers in Table III as well as in the present investigation. Hydrogen overvoltage measurements in sulfuric acid by Bowden and Rideal (31), and Jefferys, Yeager, and Hovorka (27) also have been presented in Table III. It is interesting to note that the Tafel slope is higher in sulfuric acid containing an excess of potassium sulfate. If the Tafel slope for hydrogen on nickel in sulfuric acid tends, in general, to be higher in the presence of a salt, then this may explain the slightly higher slopes obtained for hydrogen overvoltage in the present work.

The heat of activation for the discharge process at the reversible potential of the hydrogen electrode may be calculated on the basis of the following equation:

$$\Delta H^* = \alpha z F[T(\partial \eta / \partial T), -\eta]$$
 [2]

provided  $\alpha$  is independent of temperature. If this equation is applied to the data in Table I for the 0.5M nickel chloride solution at pH 2 and at temperatures of 25° and 45°,  $\Delta H^*$  is approximately +12 kcal, averaged over this temperature range. Considerable question exists, however, as to the accuracy of this value. A change in the roughness factor between 25° and 45° would cause a relatively large error. It is to be compared with values of 6.9 kcal and 16.3 kcal obtained by Bockris and Potter for 0.1N and 1.0N hydrochloric acid solutions, respectively. A knowledge of the Tafel slope, the exchange current density, and the approximate energy of activation for hydrogen overvoltage on nickel has not proved sufficient to resolve the question (32, 33) as to whether the rate-determining step is proton discharge  $(H_{aq}^{+} + e^{-} \rightarrow H_{ads})$  or electrochemical desorption  $(H_{aq}^{+} + H_{ads.} + e^{-} \rightarrow H_2)$ .

From Fig. 7 to 9, it is evident that the polarization associated with nickel electrodeposition is substantially independent of pH and follows the Tafel type dependence on current density. Deviations from linearity at higher current densities are probably associated with concentration polarization. These results support the conclusion that the rate-determining step associated with the nickel deposition is independent of hydrogen discharge over the range of conditions represented in the present work.

The apparent lack of interdependence between nickel deposition and hydrogen discharge can be explained on the basis that the number of sites available for nickel deposition does not vary appreciably with pH or potential and that the total number of sites available for each process is very large compared to the actual number of sites involved at any instant.

On the basis of the Tafel slopes listed in Table I, the value for  $\alpha z$  is approximately 0.65. Such a value appears reasonable in terms of the transfer of a nickel ion from the solution across an unsymmetrical potential energy barrier to the solid phase as the rate-determining step for the nickel polarization. If this is the case, z = 2 and  $\alpha = 1/3$ . The data in Fig. 7-9 do not appear compatible with rate-determining steps involving transfer of nickel from metastable surface sites to stable lattice sites. It is interesting to note that Yuza and Kopyl (1) in 1940 reported a Tafel slope corresponding to  $\alpha \simeq 1/2$  on the basis of oscillographic studies of nickel electrodeposition from a 1M nickel chloride solution buffered with boric acid. In 1935, Essin and Alfimova (14), primarily from current efficiency measurements, deduced a value of  $\alpha = 0.39$  for nickel sulfate over a range of concentrations and temperatures. The Tafel slope calculated from the graphs of Reiser and Fischer (7) is approximately 0.09 at 40°C for the electrodeposition of nickel from a 1.0M NiCl<sub>2</sub> - 1.0M HCl solution as well as a 0.26M NiCl<sub>2</sub> solution buffered with boric acid to pH 4.4. This Tafel slope corresponds to  $\alpha = 0.3$  for z = 2.

The variation of the cathodic potential with the nickel ion activity expressed as the derivative  $(\partial E/\partial \log a_{+})_{i}$  has been found to be 0.12 for both the chloride and the sulfate solutions on the basis of the data represented in Fig. 7. Nickel ion activities have been calculated on the same basis as described earlier in conjunction with the determination of the reversible nickel potentials. Unfortunately, present day treatments of the double layer structure are not adequate to permit a quantitative prediction of  $(\partial E/\partial \log a_{+})_{i}$  with relatively concentrated solutions of polyvalent electrolytes such as NiCl<sub>2</sub> wherein complexing occurs. Furthermore, considerable question exists as to the significance of single ion activities evaluated in such solutions by the procedure indicated earlier.

In general, the deposition of nickel from a chloride solution occurs at lower potentials with corresponding higher current efficiencies than from sulfate solutions of the same concentration. This difference between chloride and sulfate solutions is as would be predicted on the basis of the nickel ion activities for the solutions represented in Fig. 7. In the sulfate solutions, the nickel activity coefficients are considerably lower than in chloride solutions. Thus, differences between chloride and sulfate solutions are not evidence of any specific anion effects.

As in the case of the hydrogen polarization data, the energy of activation for nickel deposition may be calculated from Eq. [2], provided the surface roughness factor and  $\alpha$  are substantially independent of temperature and the method of ascertaining the reversible potential for nickel relative to the saturated calomel reference electrode is reliable. On the basis of the apparent exchange currents listed in Table I for 0.5M NiCl<sub>2</sub> at pH 2.0 for 25° and 45°C, the activation energy for nickel is +21 kcal or approximately twice that for hydrogen discharge.

A detailed discussion of the kinetics of the ratedetermining steps involved in the nickel deposition will not be given at this time but will be postponed until after the publication of later papers in this series involving the electrodeposition of nickel from mixed solvent systems and the anodic properties of nickel in simple chloride and sulfate solutions.

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# Streaming Potentials of Corundum in Aqueous Organic Electrolyte Solutions

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# ABSTRACT

The effect of certain 12-carbon anionic and cationic surface-active compounds on the zeta potential of corundum at different pH values has been evaluated from streaming potential measurements. These measurements, made under conditions of both positive and negative surface charge, indicate that long-chained ions are adsorbed appreciably only when the solid and organic ions are oppositely charged. An adsorption mechanism involving electrostatic attraction and hydrocarbon chain association is discussed using the Stern model of the double layer.

The structure of the double layer has been the subject of considerable interest during the past few years. Although most of the work published deals with theoretical considerations, a number of experimental studies utilizing electrokinetic or electrochemical techniques have also been reported. The

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effects of organic electrolytes on the properties of the electrical double layer are important in flotation and other processes dependent on surface properties, but still the technical literature on the subject is exceedingly scant. Streaming potential experiments on quartz have shown that aminium ions are strongly adsorbed and are able to change the sign of the electrokinetic or zeta potential,  $\zeta$ , because ions adsorbed

in the Stern layer associate through Van der Waals attraction between their hydrocarbon chains (1, 2)Aminium ions begin to associate at the quartz-solution interface at pH 7 when their bulk concentration is about one-hundredfold less than their bulk critical micelle concentration (2). The experiments with quartz were carried out with a negatively charged surface, but corundum offers the possibility of working with an oxide mineral that can be readily charged positively or negatively since the zero point of charge occurs at pH 9.4 (3). The object of this paper, therefore, is to present the results of an electrokinetic investigation of corundum in solutions containing long-chained organic ions under conditions of both positive and negative surface charge, and to discuss an adsorption mechanism in terms of experimental results.

#### Experimental Materials and Method

The preparation and treatment of crushed corundum and the equipment and general techniques used in this investigation have been described previously in detail (3, 4). Great care was exercised in using reagents of the highest purity. Dodecylammonium chloride was obtained from Armour and Company, Chicago, Illinois, and sodium dodecyl sulfate and sodium dodecyl sulfonate were both supplied by Colgate-Palmolive Company, Jersey City, New Jersey. A sample of pure sodium laurate was prepared by neutralizing a warm solution of recrystallized lauric acid (mp 43.3°C) in absolute alcohol with an equivalent amount of a warm solution of metallic sodium in absolute alcohol. The white, waxy precipitate which formed was filtered, washed with alcohol, and dried at 90°C.

#### **Experimental Results**

Since  $H^*$  and  $OH^-$  are potential-determining ions for alumina (3-5), the *p*H was maintained constant for each series of experiments. At *p*H values below 9.4, the alumina surface is positively charged, and at higher *p*H values it is negatively charged. Thus, by controlling the solution *p*H it is possible to study the effect of an anion or a cation on the electrokinetic potential of a positively or negatively charged surface.

Anionic organic electrolytes.—Zeta potentials of corundum were determined in aqueous solutions of sodium dodecyl sulfate, sodium dodecyl sulfonate, and sodium laurate at pH 6.5. Sodium dodecyl sulfate and sodium dodecyl sulfonate are both completely dissociated in aqueous solutions in the concentration range investigated. Since the pK of lauric acid (6) is about 5.3 and its solubility is 1.2 x $10^{-5}$  moles per liter (7), at pH 6.5 the undissociated acid should precipitate from  $2 \times 10^{-5}$ M additions of sodium laurate. The critical micelle concentrations of these anionic organic electrolytes are the following: sodium dodecyl sulfate,  $0.8 \times 10^{-2}$ M; sodium dodecyl sulfonate,  $1.0 \times 10^{-2}$ M; sodium laurate,  $2.4 \times 10^{-5}$ M.

Experimental results are presented in Fig. 1 along with measurements for sodium nitrate added for comparative purposes. The zeta potential curves are characterized by certain common features. First, the



Fig. 1. Zeta potential of corundum in aqueous solutions of sodium laurate, sodium dodecyl sulfate, sodium dodecyl sulfonate, and sodium nitrate at pH 6.5.

experimental values of  $\zeta$  indicate that all three organic electrolytes function like a simple 1:1 valent inorganic electrolyte (like NaNO<sub>s</sub>) in dilute solutions. Second, sharp breaks occur in the curves for organic electrolytes with the zeta potential becoming negative, and third, the curves contain a portion where the slope decreases again. In the case of sodium laurate solutions, however, the slope is abruptly reduced to zero by the precipitation of undissociated lauric acid. The slope of the straight line portion of the  $\zeta$ -log c curve for sodium nitrate is 17 mv, whereas for sodium dodecyl sulfate and sulfonate, it is 102 mv. For sodium laurate, it is 135 mv.

To illustrate the effect of the magnitude and sign of surface charge on the sharp break in the zeta potential curve, measurements were also made at pH 4and 11 in sodium dodecyl sulfate solutions. In Fig. 2,  $\zeta$  is plotted as a function of the concentration of both



Fig. 2. Zeta potential of corundum in aqueous solutions of sodium dodecyl sulfate and sodium chloride at pH 4, 6.5, and 11.

sodium dodecyl sulfate and sodium chloride at pH 4, 6.5, and 11. It is seen that the sharp break in the  $\zeta$ -log c curve occurs at nearly a tenfold greater dilution at pH 4 than at pH 6.5, but the slope  $d\zeta/d$  log c is still 102 mv. In contrast,  $d\zeta/d$  log c for the NaCl curves is only 17 mv and 27 mv at pH 6.5 and 4, respectively. Under conditions where corundum is negatively charged (pH 11), however, the two curves are nearly identical, the slope being -12.5mv.

Cationic organic electrolytes.—Since anionic paraffin-chain electrolytes bring about an abrupt reversal in the sign of  $\zeta$  when the surface is positively charged, it seemed reasonable that positively charged organic ions should produce similar changes under converse conditions. To study this experimentally, the zeta potential was determined in aqueous solutions of dodecylammonium chloride at pH 6.5, 10, and 11. The pK for the hydrolysis of dodecylamine is 3.4 and the solubility of dodecylamine is  $2 \times 10^{-5}$ moles per liter (8). At pH 10 and 11, the ratio RNH<sub>s</sub><sup>+</sup>/RNH<sub>s</sub> is 4.3 and 0.43, respectively. The critical micelle concentration for dodecylammonium chloride is  $1.3 \times 10^{-8}$ M.

Experimental data are presented in Fig. 3 along with data for sodium chloride added for comparative purposes. At pH 6.5, when corundum is positively charged, dodecylammonium chloride behaves as an ordinary indifferent electrolyte, such as NaCl, because identical values are obtained in solutions of equal concentration. However, when corundum is negatively charged, dodecylammonium ions abruptly change the sign of  $\zeta$  once a critical concentration is reached. For instance, in the ascending portion of the curve at pH 11,  $d\zeta/d \log c$  is nearly -350 mv. However, with further additions of dodecylammonium chloride the slope drops back to zero because of the precipitation of free amine. At pH 10, a similarly shaped curve is also obtained, although  $\zeta$  becomes somewhat less positive as more dodecylammonium chloride is added. This results from the fact that, once the solubility of the free amine is ex-



Fig. 3. Zeta potential of corundum in aqueous solutions of dodecylammonium chloride and sodium chloride at pH 6.5, 10, and 11.

ceeded, addition of dodecylammonium chloride at constant pH is equivalent to adding more NaCl, which increases the ionic strength and compresses the double layer, thereby reducing the zeta potential.

# **Discussion of Results**

Since H<sup>+</sup> and OH<sup>-</sup> are potential-determining ions for corundum (3, 5), the surface potential,  $\psi_{\sigma}$ , of corundum depends on the *p*H of the solution, and its value in volts can be calculated from

$$\psi_o = rac{kT}{ve} \ln rac{a_{\mathrm{H}^+}}{a_{\mathrm{H}_o^+}} = 0.059 \ [9.4 - p\mathrm{H}]$$
 [1]

where  $a_{H^+}$  is the activity of H<sup>+</sup> in solution and  $a_{H_a^+}$  is their activity at the zero point of charge, namely, pH 9.4 (3). In Eq. [1], k is Boltzmann's constant, Tis absolute temperature in degrees Kelvin, v is the valency of H<sup>+</sup> (sign of charge included), and e is the electronic charge. The surface potential is +300 my. +170 mv, -30 mv, and -90 mv at pH 4, pH 6.5, pH 10, and pH 11, respectively. In conductivity water, the values of  $\zeta$  should approach  $\psi_{a}$ , but surface conductance has lowered the calculated value of  $\zeta$  to +70 my because the measurements were made with particles (10, 11). Experimental measurements of  $\zeta$ with particles and capillaries made of the same glass have shown that data obtained with capillaries are 80, 50, and 17% higher in 10<sup>-6</sup>, 10<sup>-5</sup>, and 10<sup>-4</sup>M KNO<sub>3</sub> solutions, respectively, than the values determined with particles (10). However, in the present investigation, we are essentially concerned with the conditions where  $\zeta$  changes sign, and these conditions do not depend on particle size.

Monovalent inorganic electrolytes, such as NaCl or NaNO<sub>3</sub>, reduce  $\zeta$  to practically zero in highly concentrated solutions through compression of the electrical double layer (3), but under no condition do they change its sign. Monovalent organic ions, on the other hand, can change the sign of  $\zeta$  provided they are charged oppositely to the surface. Under conditions wherein the organic ion and the solid surface are charged oppositely,  $\zeta$ -log c curves indicate that organic ions are adsorbed as individual counter ions through coulombic attraction for the surface until a certain critical concentration is reached within the double layer when the hydrocarbon chains of the ions adsorbed in the Stern layer begin to associate and change the sign of  $\zeta$ . Because of the analogy of this phenomenon to micelle formation in the bulk solution, the associated organic ions in the Stern layer have been called hemi-micelles (1, 2). The reduction of the slope of the  $\zeta$ -log c curves at higher concentrations results either from monolayer coverage (in the case of dodecyl sulfate and sulfonate ions) or from precipitation of a neutral molecule (lauric acid or dodecylamine).

Stern first pointed out that the work  $W_i$  required to bring an ion from the bulk of the solution to a point in the double layer at potential  $\psi_i$  might involve not only electrostatic work

$$W_i = v e \psi_i$$
 [2]

but also chemical work, 
$$\phi$$
:  
 $W_i = ve \psi_i - \phi$  [3]
If the adsorbed ion possesses a long hydrocarbon chain, Van der Waals association between hydrocarbon chains of similarly adsorbed ions will give rise to an additional work term,  $\phi'$ :

$$W_i = ve\,\psi_i - \phi - \phi' \qquad [4]$$

From the data presented in Fig. 2 and 3, it can be seen that reversal of  $\zeta$  occurs only when the solid and organic ion are oppositely charged, meaning that the organic ions are adsorbed appreciably only when they can function as counter ions at the interface. Since these long-chained electrolytes affect  $\zeta$  in a manner identical to any indifferent electrolyte under conditions of like charge, they have no chemical affinity for alumina and, consequently for this system,  $\phi$  is zero. Thus, the inner Helmholtz plane will be empty and the heads of the adsorbed organic ions will lie in the outer Helmholtz or Stern plane. Under conditions represented by the initial portion of the  $\zeta$ -log c curves, the force of adsorption is simply electrostatic and  $\phi'$  is zero, whereas under conditions corresponding to the second and third parts of the curves, Van der Waals force of association between hydrocarbon chains becomes operative and  $\phi'$  has a finite value. However,  $\phi'$  is not constant and will depend on the orientation of the adsorbed organic ions in the Stern layer. Thus, the attractive force between the adsorbed organic ions will increase from zero to a value that is approximately the energy gained by taking the hydrocarbon chain out of water; namely, 1.1 kT per CH<sub>2</sub> group in the chain (9). The rate at which  $\phi'$  becomes effective is illustrated qualitatively by any of the graphs.

Qualitatively, dodecyl sulfate ions change the sign of  $\zeta$  at a lower bulk concentration than is required for dodecyl sulfonate ions, which is in accord with their relative critical micelle concentrations. However, even though the critical micelle concentration of sodium laurate is somewhat higher than that for sodium dodecyl sulfate, laurate ions begin to associate at the corundum-solution interface at a lower bulk concentration than is required for sodium dodecyl sulfate. At pH 6.5, the ratio of laurate ions to lauric acid molecules in solution is 16, that is, nearly 6% of the sodium laurate added is present as undissociated lauric acid. In the bulk solution this concentration of 12-carbon neutral molecules is not sufficient to lower the cmc (12), but it must be a major factor in adsorption at the solid-solution interface. If a laurate ion is anchored in the Stern plane, a lauric acid molecule can then be adsorbed through association of hydrocarbon chains. Another laurate ion can then be adsorbed through Van der Waals attraction between its hydrocarbon chain and that of an anchored lauric acid molecule. In this case repulsion between the charged laurate ion heads will be lower because of the intervening uncharged molecule. This is rpresented by Frep in Fig. 4. If association of organic molecules with organic ions takes place before the Stern layer is sufficiently populated with enough organic ions for the ions to associate by themselves,  $\phi'$  should already have a finite value when the curves begin to break sharply. Observation of Fig. 3 shows that the  $\zeta$ -log c curves



Fig. 4. Schematic representation of double layer when neutral molecules are present.

for dodecylammonium chloride (pH 10 and 11) begin to deviate from the curves for NaCl at concentrations above  $2 \times 10^{-6}$ M. This deviation increases gradually until it is 12 mv at the point where the  $\zeta$ -log c curve breaks sharply. Thus,  $\phi'$  for the system involving dodecylammonium chloride in alkaline solutions is zero only until  $2 \times 10^{-6}$  mole of the organic salt has been added. Because of the presence of the dodecylamine molecules,  $\phi'$  begins to increase gradually for  $2 \times 10^{-6}$ M additions, but it increases sharply at the abrupt break in the  $\zeta$ -log c curves. If the organic salt is a strong electrolyte, organic molecules are absent and the  $\zeta$ -log c curves do not deviate from those of NaCl before the sharp break (Fig. 2).

Increasing the surface potential, that is, lowering the pH from 6.5 to 4.0, was found to reduce the bulk concentration of dodecyl sulfate ions which is required for the adsorbed ions to associate (Fig. 2). This results from the increased adsorption of counter ions. It should be pointed out that competition exists for sites in the double layer because the concentration of Cl<sup>-</sup> is 10<sup>-4</sup>M. At pH 11, sodium dodecyl sulfate affects  $\zeta$  in a manner identical to sodium chloride. This indicates that the counter ions in each case are sodium ions and that dodecyl sulfate ions have no chemical affinity for corundum. In this case no association can take place because the concentration of dodecyl sulfate ions next to the surface is only about one-tenth of the bulk concentration.

A quantitative estimate of the value of  $\phi'$  can be made by looking at the double layer under conditions where  $\zeta$  is zero. For this quantitative treatment, the Stern plane must be assumed to coincide with the shear plane in streaming experiments in order that  $\zeta$  equals  $\psi_s$ , the potential at the Stern plane. Under conditions where  $\zeta$  is zero, all the counter ions occur in the Stern plane and consequently the double layer consists only of a molecular condenser.

The capacity  $C_s$  of the molecular condenser will be assumed to be constant and the relation with the surface charge  $\sigma$  where  $\zeta$  is zero can be expressed by

$$\sigma = \psi_o C_s$$
 [5]

The charge of the Stern plane,  $\sigma_s$ , which is equal to but opposite in sign to the surface charge for this

Table I. Data for the calculation of  $\phi'$  with Eq. [8a] when  $\zeta$  is zero

pH	$\psi_o$ , mv	y	K,	Co	$\phi', kT$
6.5	+170	6.8	10.9	$8.2 imes10^{-5}{ m M}$	8.9
4.0	+300	12	10.9	$3.3 imes10^{-5}$	10.9
11.0	-90	-3.6			0
6.5	+170	6.8	10.9	$1.2 imes10^{-4}$	8.6
6.5	+170	6.8	22.2	$2.5 imes10^{-5}$	9.4
6.5	+170	6.8			0
10.0		-1.3	21.2	$8.9 imes10^{-5}$	6.9
11.0	90	-3.6	21.2	$1.2 imes10^{-5}$	9.5
	pH 6.5 4.0 11.0 6.5 6.5 6.5 10.0 11.0	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

model, is given by

$$\sigma_s = 2 \ rnve \ \exp\left(\frac{\phi'}{kT}\right)$$
 [6]

11 \

when  $\zeta$  is zero (13). In Eq. [6] r is the radius of the ion under consideration, that is, the head of the organic ion charged oppositely to the surface, and n is the number of such ions per cc of bulk solution.

For the molecular condenser:

$$\psi_{\sigma} C_s = \sigma = -\sigma_s = -2 \ rnve \ \exp\left(rac{\phi}{kT}
ight)$$
 [7]

Multiplying both sides of the equation by ve/kTand rearranging terms gives

$$\frac{ve\,\psi_{*}}{kT} = -\left(\frac{ve}{kTC_{*}}\right)2\,rnve\,\exp\left(\frac{-\phi'}{kT}\right)\quad [8]$$

$$vy = -K c_{\circ} \exp\left(\frac{\phi'}{kT}\right)$$
 [8a]

where y is  $e\psi_o/kT$  ( $\psi_o$  being evaluated from Eq. [1]),

K. is 
$$\frac{2 v^2 e^2 r}{kTC_s}$$
 (N/1000). Here N is 6.02 x 10<sup>23</sup> mole-

cules per mole, and c, is the concentration in moles per liter of the organic electrolyte to bring the value of  $\zeta$  to zero. Evaluation of  $\phi'$  depends on the value and constancy of  $C_s$ , the mathematical identity of the Stern plane and the shear plane (obviously the shear plane exists outside the hydrocarbon chains of the adsorbed organic ions, but for use of Eq. [8]  $\psi_s$  must be zero when  $\zeta$  is zero), and the presence or lack of a layer of water molecules between the adsorbed ions and the surface. For the present calculation, the large sulfate and sulfonate ion (2.9Å radius) will be considered to be dehydrated, and consequently the capacity of the Stern layer will be about 25  $\mu$ F/cm<sup>2</sup>. Because of the similarity in behavior between ammonium ions and the aminium ions (2), the aminium ions are probably separated from the surface by a layer of water molecules and  $C_s$  will thereby be about  $15\mu F/cm^2$  (14). The value of r in Eq. [8] then must be the radius of the aminium head plus one water molecule, or a total of 4.2Å. Similarly, the relatively small soap ion (which would be 1.7Å when the tail is perpendicular to the surface) will be considered to be separated by a layer of water molecules from the surface. Consequently, the value of r in Eq. [8] will be 4.4Å and  $C_s$  will be  $15\mu F/cm^2$ .

The results of calculating  $\phi'$  with Eq. [8] when  $\zeta$  is zero are presented in Table I. The concentration of dodeclyammonium ions must be corrected to account for hydrolysis at pH 10 and 11.

In our picture of the adsorption mechanism, the adsorption potential  $\phi'$  is zero until the organic ions in the Stern layer begin to associate, this being depicted by the deviation of the  $\zeta$ -log c curve of an organic electrolyte from a surface-inactive inorganic electrolyte. For example, in the system involving corundum in aqueous solutions of sodium dodecyl sulfate at pH 6.5,  $\phi'$  will be zero until the bulk concentration of sodium dodecyl sulfate reaches 10<sup>-5</sup>M. Thereupon,  $\phi'$  begins to increase as the adsorbed ions associate, reaching a value of about 8.9 kT when the bulk concentration is 8 x10<sup>-5</sup>M. Under these conditions  $\zeta$  is zero. The value of  $\phi'$  will continue to increase until the Stern layer is filled. Under these conditions  $\phi'$  will approach 12 kT if all but the end CH<sub>3</sub> group is out of water. Beyond this point, adsorption probably will occur in multilayers. A plot of  $\phi'$  vs. the logarithm of the concentration of sodium dodecvl sulfate yields a fairly straight line if  $\phi'$  is zero at the first break in the  $\zeta$ -log c curve (10<sup>-5</sup>M), 8.9 kT when  $\zeta$  is zero (8 x 10<sup>-5</sup>M), and 12 kT at the second break in the  $\zeta$ -log c curve (3 x 10<sup>-4</sup>M). The slope of this curve  $d\phi'/d \log c$  is about 9 kT. A similar plot of the data at pH 4 shows that  $d\phi'/d \log c$  is reduced to about 7 kT. This reduction probably reflects the competition between dodecyl sulfate ions and chloride ions at the surface. For sodium laurate,  $d\phi'/d \log c$  is about 8 kT. Since the solubility limit of dodecylamine is rapidly reached,  $d\phi'/d \log c$  is over 300 kT (note the steep slopes in Fig. 3) for the systems involving dodecylammonium chloride at pH 10 and 11.

In this paper, the adsorption potential  $\phi'$  which arises through association of hydrocarbon chains has been evaluated by considering the double layer as a molecular condenser when  $\zeta$  is zero. Since  $\phi'$  appears as an exponent in Eq. [8], its value does not change appreciably with the change in capacity of the Stern layer. However, adsorption measurements should be carried out to determine the actual value of the capacity of the molecular condenser in order to ascertain whether the organic ions are hydrated or not in the Stern layer.

#### Summary

The effect of 12-carbon organic ions on the zeta potential of corundum has been measured by stream-

ing potential techniques. Experimental data indicate that organic ions are adsorbed appreciably only under conditions where the solid and the organic ions are charged oppositely. Adsorption takes place as individual ions until a sufficiently high concentration is attained in the Stern layer to permit association of their hydrocarbon chains. This association results in increased adsorption which can be represented by an adsorption potential in the Boltzmann equation. By considering the double layer to be a molecular condenser when  $\zeta$  is zero, the adsorption potential resulting from association of hydrocarbon chains was evaluated. The presence of uncharged long-chained molecules reduces the bulk concentration required for association next to the surface.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1959 JOURNAL.

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## **Capacities of Solid Metal-Solution Interfaces**

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## ABSTRACT

An electric analog of the metal-solution interface was assumed and E vs. t changes were deduced mathematically for application of a square wave voltage. The analysis was verified using actual electric components, and it was demonstrated that the component of capacity could be measured readily. The method was applied with some success to each of the following systems: mercury in 0.1N Na<sub>2</sub>SO<sub>4</sub>, platinum, silver, copper, aluminum, and tantalum in 1N Na<sub>2</sub>SO<sub>4</sub>.

At various times investigators have attempted to determine roughness factors (ratios of true to apparent surface areas) of metal electrodes by means of capacity measurements. Assumptions usually made in these attempts included (*a*) that all metals have the same capacities at potentials slightly anodic (positive) to their hydrogen evolution potentials, and (*b*) that for mercury the apparent surface area is the true surface area. Thus if the capacity per square centimeter of apparent area for the metal M was  $C_{\rm M}$  (at a potential just short of hydrogen evolution) and that for mercury  $C_{\rm Hg}$  (at a similar potential) then the roughness factor of the metal M was  $C_{\rm M}/C_{\rm Hg}$ .

Assumption (b) is reasonable. However, assumption (a) is not entirely tenable. The small amount of information in the literature concerning capacities of solid metal electrodes shows wide discrepancies. Grahame (1) has published very useful papers con-

cerning the differential capacity of mercury. Solid metal electrodes, however, have not been investigated systematically. Of course, differential capacities of solid electrodes cannot be checked by electrocapillary methods and as a result electrical double layer (edl) theory concerning solid metal electrodes has not been as extensively treated as has that of the mercury-solution system.

Several experimental techniques have been utilized to measure differential capacities of mercurysolution interfaces. The most sensitive method is the impedance bridge method. Grahame (1) has used this method extensively and reports an accuracy of better than 1%. The major drawback of this method is its inapplicability to large capacities. Bowden and Rideal (2) devised a method of measuring capacities by direct charging. They observed the potential change resulting from the passage of a known direct current for a known length of time. The potential changes involved, however, were of the order of 0.5 v, and the capacities calculated were, therefore, an

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Fig. 1. Circuit diagram

average over a large potential change. Wagner (3) used a ballistic galvanometer to measure the charge required to polarize a silver specimen 0.1 v.

Methods involving direct charging all assumed that any current supplied to the electrode was involved in charging the edl. In effect, the assumption was made that the interface behaved as an ideally polarizable one.

Brodd and Hackerman (4) reported results obtained with solid metal electrodes showing a correlation between areas calculated from capacity data and areas measured by krypton adsorption. Their capacity data were obtained from time-potential traces observed when a square-wave signal was applied to the electrodes. This method has been modified and utilized here in an attempt to determine the differential capacity curves for several solid metal-solution interfaces.

#### Experimental

The circuit diagram is shown in Fig. 1. The source of the square wave voltage was a Model 202-A function generator manufactured by Hewlett-Packard. The generator applied a square wave voltage, across the series resistance,  $R_{*}$ , to the electrodes N and M. The potential change across the cell was observed on the cathode-ray oscilloscope, CRO. Potentiometer  $P_1$  was used to polarize electrode M using N as an auxiliary electrode. Potentiometer  $P_2$  measured the potential of M with respect to the saturated calomel electrode, SCE. L was an inductance placed in the circuit to keep the alternating current from the di-



rect current parts of the circuit. For each measurement the CRO was connected to the generator to obtain a trace of the input square wave. Permanent records of the traces were obtained photographically.

The Pyrex cells used for measurements and for reservoir are, respectively, A and B in Fig. 2. The mercury electrode M was formed in a Pyrex cup with an inside diameter of 2.5 cm. The mercury level was controlled so that the top of the mercury meniscus was tangent to the plane at the top of the cup. A fresh surface was obtained by overflowing the mercury from the cup. A platinized platinum screen cylinder, N, suspended through the top of the cell and surrounding the mercury electrode, was in series with the mercury electrode in the a-c circuit. The area of the platinum screen cylinder was very large compared to that of the mercury; hence its capacity was large and its effect on the cell impedance should have been negligible. The saturated calomel electrode, SCE, was immersed in the solution in a small side cell connected to the main cell A through the closed stopcock S<sub>2</sub>.

A ball joint and closed stopcock  $S_1$  connected the main cell A with cell B. Cell B served as a preelectrolysis cell and reservoir for solution. Pre-electrolysis with a current of 3 ma was carried out for at least 12 hr.

Bureau of Mines grade A helium, reported as 99.99% pure, was bubbled through a saturator and passed into cells A and B. The helium stirred the solution and provided an inert atmosphere. After pre-electrolysis and at least 4 hr of helium flushing, the helium pressure was used to force solution from B into A.

Distilled water was redistilled from alkaline permanganate to remove any organic matter. The mercury was triple-distilled instrument mercury. Other metals were used as wires put into the solution through the tip of the cell. Pretreatment of wires consisted of degreasing, washing with dilute sulfuric acid, and rinsing with distilled water.

The importance of avoiding grease contamination has been demonstrated (5). No grease was used in any part of the apparatus employed in these experiments.

Analysis of time-potential curve.—In the study of time-potential curves obtained with a square wave, it is helpful to consider the time-potential changes at the electrode surface in terms of an analogous electric circuit. Various simple and complex arrangements of resistors and capacitors have been utilized to represent the behavior of such an interface. One of the simplest, Fig. 3, consists of a condenser (C) in parallel with a resistance  $(R_r)$ , both being in series with another resistance  $(R_r)$ . In the present case the square wave passed through resistance R, before entering the cell. The potential difference between points A and B was observed on the



Fig. 2. Polarization cell and reservoir

Fig. 3. Electric analog circuit

CRO. Three cases were examined to determine the time-potential behavior to be expected under different conditions.

Case I: 
$$R_p = \alpha$$
;  $R_c = 0$ 

If the simplifying assumptions are made that the interface is an ideally polarizable one and that the resistance of the solution is zero, then  $R_p$  is infinite and  $R_e$  is zero. The equation for the change of voltage  $(E_c)$  between points A and B, in this case, is

$$E_{c} = E_{i} [1 - \exp(-t/R_{s}C)]$$
 [1]

where t is time and  $E_t$  is the input voltage. The value of  $E_c$  approaches the value of the input voltage, exponentially, with increasing time. At short time intervals,  $t \ll R_sC$ , the exponential in Eq. [1] was expanded to give

$$E_c = E_i t / R_s C$$
 [2]

In this time interval  $E_c$  is a linear function of time. With reversal of the current, i.e., on the second half of the square wave cycle, another linear function, with slope of opposite sign, is obtained. The composite result for small time intervals is a triangular trace on the CRO.

Case II:  $R_p \neq \alpha$ ;  $R_c = 0$ 

If the interface is not an ideally polarizable one,  $R_{\nu}$  has a finite value. The equation for the change in voltage is now:

$$E_{e} = \frac{E_{i}R_{p}}{(R_{s} + R_{p})} \left[ 1 - \exp \frac{\{-t(R_{p} + R_{s})\}}{CR_{p}R_{s}} \right] \quad [3]$$

At short time intervals,  $t \ll R_*/(R_p + R_*)$ , the exponential in Eq. [3] was expanded to give Eq. [2]. The form of the trace is thus the same as in Case I.



Fig. 4. Traces obtained for analogs (see text for explanation)

Case III: 
$$R_p \neq \alpha$$
;  $R_e \neq 0$ 

Introduction of  $R_e$  into the system results in discontinuities in the time-potential curve. These potential drops are representative of  $IR_e$ , where I is the current. The equation of each half-cycle obtained on the oscilloscope is thus:

$$E_e = IR_e + E_i t / R_s C \qquad [4]$$

In all three cases, therefore, Eq. [2] gives the dependence of  $E_c$  on t for small values of time. Differentiating Eq. [2] with respect to time gives

$$dE_c/dt = E_i/R_sC$$
 [5]

If the frequency of the input square wave is selected to give a triangular trace on the oscilloscope, then the absolute values of the slope for each halfcycle is given by Eq. [5].

The three cases given above were studied experimentally by obtaining oscilloscope traces for the respective electrical circuits.

Figure 4a is a photograph of the CRO trace for the time-potential curve with the circuit described in Case I (Fig. 3). Here C was a  $37\mu$ F commercial electrolytic condenser,  $R_*$  was a 15,000-ohm resistor, and the input voltage,  $E_i$ , was 100 cps square wave. A trace of the input voltage  $E_i$ , attenuated 100:1, is shown in Fig. 4b.

From the slope of the trace in Fig. 4a, and the known values of the input voltage  $(E_i)$  and of  $R_i$ , the capacity of condenser C can be calculated with Eq. [5]. The time for one half-cycle was 0.005 sec; the voltage rose 10 divisions in this time, giving the slope 2 x 10<sup>3</sup> div./sec. Therefore,

C = 
$$(dt/dE_c) (E_i/R_s) = \left(\frac{1}{2 \times 10^3}\right) \frac{12(100)}{15,000} = 40 \mu F$$

This is in good agreement with  $37\mu F$  measured by the conventional bridge method.

Figure 4c shows a trace obtained with a circuit described under Case II. Here, C was a  $54\mu$ F condenser,  $R_{p}$  a 100-ohm resistor,  $R_{s}$  a 15,000-ohm resistor, and the frequency 50 cps. The time-potential curve is not a triangular wave. However, when the frequency of the input square wave was increased to 500 cps the output trace was triangular and the calculated capacity was  $58\mu$ F. An increase in the amplitude of the input square wave, at this same frequency, resulted in a triangular trace with increased slope, and looked just like the trace in Fig. 4a. The product of the reciprocal of the slope and the input voltage remained constant, however, and the calculated capacity was again  $58\mu$ F.

Figure 4d shows a trace obtained with a circuit described by Case III. Here C was a  $54\mu$ F condenser,  $R_{\mu}$  100 ohms,  $R_{\star}$  15,000 ohms,  $R_{\star}$  13 ohms, and the frequency 500 cps. The time-potential curve showed discontinuities between the linear portions. The calculated capacity was  $58\mu$ F. The  $IR_{\star}$  drop, (Fig. 4d), was 1.5 divisions. When  $R_{\star}$  was doubled to 26 ohms, the discontinuity doubled in size (Fig. 4e) to 3 divisions. The calculated capacity remained the same, since the slope of the linear portions did not change.

## **Results and Discussion**

*Mercury.*—The mercury-solution interface was investigated as another check, since the results could be compared with those of other workers. The Pyrex cup containing the mercury had an inside diameter of 2.5 cm. Assuming the surface of the mercury to be planar, the surface area was 5 cm<sup>2</sup>. If the curvature of the surface were taken into consideration, the area could be as high as 6 cm<sup>2</sup>. The former value was used here.

The solution used was 0.1N Na<sub>2</sub>SO,, and all experiments were conducted at  $30^{\circ} \pm 1^{\circ}$ C. The potential values given refer to the saturated calomel electrode. A 15,000-ohm resistor was used as the series resistance *R*, throughout the rest of the experiments. Application of the square wave voltage, employed to carry out the capacity measurements, changed the potential of the electrodes somewhat. The change of potential was less than 10 divisions on the CRO. Since the sensitivity of the CRO was approximately 1.5 mv/division, the uncertainty in the measured potentials of the electrodes were less than 0.02 v.

Figure 5a is a photograph of a typical time-potential trace obtained with mercury electrodes. The potential of the mercury was -0.2 v in this case. The time-potential trace is a triangular wave with discontinuities between the linear portions. This type of trace corresponds to Case III. The calculated capacity was  $154\mu$ F or  $31\mu$ F/cm<sup>2</sup>.

Capacity measurements were made at potentials varying from 0.0 to -1.0 v. These potentials were obtained by polarizing the mercury electrode with an auxiliary potentiometer. The differential capacity curve is shown in Fig. 6.

Grahame (1) found the potential at the zero point of charge (zpc) of mercury in 0.1N Na<sub>2</sub>SO, to be -0.44 v. Therefore, for the purposes of discussion, the curve in Fig. 6 may be divided into three re-



Fig. 5. (a) Trace obtained with Hg electrode. (b) Trace obtained with Pt electrode.



Fig. 6. Differential capacity curve for Hg-0.1N Na<sub>2</sub>SO<sub>4</sub>

gions: (a) a region of potentials more negative than the zpc (cathodic branch of the curve), (b) a region of potentials more positive than the zpc (anodic branch of the curve), and (c) a region of potentials in the immediate vicinity of the zpc.

The capacity on the cathodic branch is independent of the potential and has a constant value of 19  $\mu$ F/cm<sup>2</sup>. This value would be 16 $\mu$ F/cm<sup>2</sup> if the higher surface area value were used. The constancy of the capacity along this branch of the curve has been verified experimentally many times. The value obtained here agrees with Proskurnin and Frumkin (6), Barclay and Butler (7), and Philpot (8). Grahame's experimental value was 16 $\mu$ F/cm<sup>2</sup>.

The anodic branch of the curve does not show the broad flat portion found on the cathodic branch. However, for a narrow region of potentials, the curve has a slope close to zero. The average capacity in this region was about  $33 \mu F/cm^2$ . Grahame's curve shows such a "hump" at about  $35 \mu F/cm^2$ .

In the region of the zpc, a transitional portion of the curve occurs with capacities intermediate between those for the cathodic and anodic branches of the curve. In very dilute solutions (N/100 and less), this region exhibits a more or less sharp minimum. Even with 0.1N Na<sub>2</sub>SO<sub>4</sub> Grahame found a minimum of the order of 1 or  $2\mu F/cm^2$ . The sensitivity of the present measurements is insufficient to permit observation of such a shallow minimum in the curve.

Platinum.—In order to avoid the large solution resistance encountered in dilute solutions, the remaining experiments were conducted in  $1N \text{ Na}_2\text{SO}_4$ . The platinum electrodes were 20 cm in length and were cut from smooth wire having a diameter of 0.04 cm. The apparent electrode area was 2.5 cm<sup>2</sup>.

A photograph of a typical time-potential trace obtained with platinum electrodes is shown in Fig. 5b. The time-potential trace is again of the type discussed under Case III above. However, the  $IR_e$  drop is considerably less than with mercury in 0.1N Na<sub>2</sub>SO<sub>4</sub> (compare Fig. 5a and 5b).

Results of the capacity measurements, at potentials varying from 0.0 to 1.4 v, are shown in Fig. 7. The shape of the curve obtained is similar to that for mercury. Three regions are evident: a portion where the capacity is fairly constant at approximately  $80\,\mu\text{F}$ , a narrow region having a capacity of



Fig. 7. Differential capacity curve for Pt-1N Na<sub>2</sub>SO<sub>4</sub>. (Apparent area 2.5 cm<sup>2</sup>.)

approximately  $58\,\mu\text{F}$ , and a connecting portion with intermediate capacities.

These regions can be interpreted in the same fashion as for the curve obtained for mercury in 0.1N Na<sub>2</sub>SO<sub>4</sub>. The transitional portion of the curve is expected to be in the neighborhood of the zpc. Therefore, the zpc for platinum in this solution should be  $0.5 \pm 0.2$  v. Robertson (9) has obtained a capacity minimum, for platinum in 1N HCl, at 0.79 v. A value of -0.04 v in acidified 1N Na<sub>2</sub>SO<sub>4</sub> by contact angle measurements has also been reported (10).

The cathodic portion of the curve, with total capacities of the order of  $54 \,\mu\text{F}$ , is the region of cation predomination in the double layer. Using the apparent area of the electrodes, the capacity was approximately  $22 \,\mu\text{F/cm}^2$ . On the anodic portion the capacity was  $32 \,\mu\text{F/cm}^2$ .

Silver.—The apparent area of the silver electrodes was 1.3 cm<sup>2</sup>. The polarization caused by the square wave voltage was less than 15 mv.

The results of capacity measurements, at potentials of 0.0 to -1.2 v, are shown in Fig. 8. The shape of the curve is similar to that obtained for the mercurv-solution interface. The zero point of charge has been reported for silver, in 0.1N KNO<sub>3</sub>, as -0.233v (11). A hump appears, in the vicinity of this potential, on the capacity-potential curve. Similar humps have been observed in the region of the zero point of charge for capacity-potential curves obtained for mercury in concentrated solutions. Grahame (1) has suggested that the humps arise from the mutual electrostatic repulsion of ions in the double layer. Watanabe, Tsuji, and Ueda (12) have suggested that this phenomenon is related more to mercury-ion interaction than to ion-ion interaction. The appearance of this phenomenon with silver and not with platinum seems to favor the latter suggestion.

The cathodic portion of the curve shows a capacity of approximately  $58\,\mu\text{F}$ . This would be the



Fig. 8. Half-filled circle: Differential capacity curve for Ag-1N Na<sub>2</sub>SQ., (Apparent area 1.3 cm<sup>3</sup>.) Open circle: Differential capacity curve for Al-1N Na<sub>2</sub>SQ., (Apparent area 2.5 cm<sup>3</sup>.) Solid circle: Differential capacity curve for Al-1N Na<sub>2</sub>SQ, after cathodic treatment.

region of cation predomination in the solution side of the double layer. The capacity was approximately  $45 \,\mu$ F/cm<sup>2</sup>. This apparently high value of the capacity is not unreasonable. Wagner (3) has reported values of the order of  $100 \,\mu$ F/cm<sup>2</sup> for "smooth" silver wires.

Aluminum.-The apparent surface area of the aluminum electrodes was 2.5 cm<sup>2</sup>. The results of capacity measurements are shown in Fig. 8. The shape of this curve has no similarity to the curve obtained for mercury. The capacity is fairly constant over the range of potentials at which it was measured. The low values of the capacities, about  $3 \mu F/cm^2$  of apparent surface, are not surprising, since aluminum is normally covered with an oxide film. Rakov and Ershler (13) obtained  $7 \mu F/cm^2$  for an oxide covered electrode. The capacity of the oxide film is small compared to the capacity of the double layer. Therefore, the measured capacity would be primarily that of the oxide film. The capacity of the film is not dependent upon the potential. This explains the apparent nondependence of the measured capacity upon the potential.

Estimates of the thickness of oxide films on metals have been made by capacity measurements (14). Wanklyn (15) has used capacity measurements to study the protective character of oxide films on zirconium alloys. In these measurements the double layer capacity was neglected. Assuming the film substance to be  $\gamma Al_2O_{5}$ , and using a value of 8 for the dielectric constant (16), the film thickness was calculated to be approximately 20Å.

A potential large enough to evolve hydrogen at the aluminum electrode was applied, momentarily, between it and an auxiliary electrode placed in the small side cell. The capacity was measured at potentials progressively more anodic. The results of these measurements are shown in the upper curve in Fig. 8. The capacity was found to be much higher after this treatment but decreased with time and the potential of the aluminum became progressively more anodic. The values of the capacity after cathodic treatment were in all cases substantially higher but fairly irreproducible. It is likely that the rise in capacity after cathodic pretreatment may be caused by the oxide film thinning due to the local increase in pH at the electrode.

Tantalum.—The apparent area of the tantalum electrodes was 1.6 cm<sup>2</sup>. The results of the capacity measurements are shown in Fig. 9. The shape of this curve is very similar to that of aluminum. Tantalum, like aluminum, is normally covered by an oxide film. Therefore, the low values obtained for the capacities are in no way unusual. The average value of the capacity was approximately  $9\,\mu$ F/cm<sup>2</sup>. Capacities were measured at progressively more anodic potentials to observe possible evidence of increased oxide formation. From Fig. 9 it can be seen that there is a continuous slow trend toward lower capacities. This lowering of capacity at more anodic potentials suggests the formation of more oxide on the surface of the tantalum.

Copper.-The apparent surface area of the copper



Fig. 9. Open circle: Differential capacity curve for Ta-IN Na<sub>2</sub>SO<sub>4</sub>. (Apparent area 1.6 cm<sup>2</sup>.) Solid triangle: Differential capacity curve for Cu-IN Na<sub>2</sub>SO<sub>4</sub>. (Apparent area 2.4 cm<sup>2</sup>.)

electrodes was 2.4 cm<sup>2</sup>. The capacity-potential curve is shown in Fig. 9.

Since no value of the zpc could be found in the literature, an approximation method, as used earlier by Brodd and Hackerman (4), was tried. The work function for copper is 4.6 ev (17) and for mercury 4.5 ev (18). The difference between these two is 0.1 v. The zpc for mercury is -0.44 v; therefore, the zpc for copper is approximately -0.3 v. It is further noted that this approximation is made more approximate because of the variations in the values of the work functions found in the literature.

The capacity-potential curve (Fig. 9) shows a minimum of capacity at a potential of about -0.3 v. The shape of the curve is similar to that of mercury in that the capacity goes through a minimum. The anodic branch is similar to the anodic branch of the curves obtained for mercury in solutions containing anions which specifically adsorb (1). The results indicate that sulfate ion has specifically adsorbed on the copper.

The cathodic portion of the curve does not display a broad flat minimum as with mercury. The rise in capacity occurs with mercury but at much more cathodic potentials. This difference could be accounted for by the high hydrogen overvoltage on mercury and the smaller overvoltage on copper.

The minimum of capacity corresponds to  $21 \,\mu\text{F}$ cm<sup>2</sup>. Winkler (19) reported a capacity of  $23 \,\mu F/cm^2$ for cathodic charging of copper.

### Conclusions

The results obtained for electric analogs and the agreement of the results obtained for the mercurysolution interface with those of other workers attest to the reliability of the method.

The shapes of the differential capacity curves reported indicate that for most metals only a limited potential range is available for capacity measurements from which to estimate surface areas.

The capacity-potential curves obtained for film covered metals, aluminum and tantalum, suggests the applicability of the method to film formation and film removal studies. Further work along these lines is underway.

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# Preparation and Properties of Improved Protamine Collodion Matrix Membranes of Extreme Ionic Selectivity

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#### ABSTRACT

Improved protamine collodion matrix membranes of extreme electrochemical activity were prepared by the adsorption of purified protamine from aqueous solutions on preformed highly porous collodion membranes whose porosity was subsequently reduced by drying. The most useful permselective membranes give rise to concentration potentials which agree with the calculated thermodynamic maximum potential in potassium chloride cells up to 0.1N/0.05Nwithin the meaningfulness of the method. At higher concentrations the measured potentials become gradually less than the theoretical value. The more highly selective membranes have anion permeabilities which in 0.1N KCl are 250 to 450 times greater than the cation permeabilities and 2,000 to 12,000 times greater in 0.01N solutions. With solutions of CaCl<sub>2</sub> these ratios were at least two orders of magnitude greater. The ohmic resistances of the permselective membranes of highest selectivity (as measured in 0.1N KCl) may be adjusted from about 10 ohm-cm<sup>2</sup> upward.

The first membranes which combined a high degree of anionic selectivity with great stability and low resistance were the permselective protamine collodion matrix membranes described by Carr, Gregor, and Sollner (1-5).<sup>2</sup> They were prepared by the adsorption of protamine from buffered ( $\cong pH 10.5$ ) aqueous protamine sulfate solutions on collodion membranes of high porosity which were subsequently dried under carefully controlled conditions. The most important shortcoming of these membranes was their limited ionic selectivity; their permeabilities for anions even at concentrations as low as 0.01 and 0.001N were only 30-50 times greater than those for cations. This low ratio severely restricts the usefulness of these membranes in many studies.

Anion selective membranes of high resistance have been prepared by Albrink and Fuoss (6). Membranes of the permselective type were described in recent years by Bonhoeffer and Manecke (7), Winger, Bodamer, and Kunin (8), Wetstone and Gregor (9), and others (10-12). For our purpose these membranes have somewhat too low ionic selectivities, especially at higher concentrations, and too high unit area exchange capacities. Also the porosities and resistances of these membranes cannot be as readily adjusted at will as those of collodion matrix membranes.

Collodion matrix membranes of extreme anion selectivity which are free from these limitations and

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shortcomings were prepared some years ago in this laboratory by the adsorption from aqueous solution of poly-2-vinyl-N-methylpyridinium bromide (and several other basic synthetic polyelectrolytes) on preformed highly porous collodion membranes whose porosity was subsequently reduced by drying (13). The most useful of these membranes give rise to concentration potentials which agree closely with the calculated thermodynamic maximum potentials in potassium chloride cells up to 0.1N/0.05N. The more highly selective membranes have anion permeabilities which in 0.1N KCl are 500-1300 times greater than the cation permeabilities, and in 0.01N solutions 5,000-32,000 times greater. With solutions of CaCl<sub>2</sub> these ratios are two to three orders of magnitude greater. The ohmic resistances of these membranes as measured in 0.1N KCl may be adjusted from about 10 ohm-cm<sup>2</sup> upward (13). While otherwise fully satisfactory for many physicochemical investigations and model studies of biological interest, these membranes quite unexpectedly show a peculiarity which restricts their usefulness for certain purposes. The rates of self-exchange of critical ions between solutions across these membranes do not agree with those calculated from the Nernst-Einstein equation, whereas this equation describes satisfactorily the results of self-exchange studies with protamine collodion matrix membranes, or with (cation selective) oxidized collodion and sulfonated polystyrene collodion matrix membranes (14).

In order to prepare anion selective membranes of extreme ionic selectivity which behave in the manner postulated by the Nernst-Einstein equation with respect to the rate of exchange of ions across them, it seemed best to try to improve the ionic selectivity of the otherwise satisfactory protamine collodion

<sup>&</sup>lt;sup>2</sup> Protamines are simple strongly basic proteins, ordinarily derived from salmon sperm, with molecular weights of about 4000 in the hydroxyl form. They are of somewhat varying composition, most probably consisting of nineteen molecules of arginine, a dibasic amino acid with a pK of 10.5 to 11, and six or seven monobasic amino acids. The ionizable groups in the protamine molecule, which are not blocked by the formation of peptide linkages, are: one carboxyl group, one imino group, and nineteen guanidino groups.

matrix membrane. This seemed desirable also in view of the planned use of these membranes in studies of biological interest because the chemical nature of protamine is more similar to that of biological membranes than that of synthetic polyelectrolytes, such as poly-2-vinyl-N-methylpyridinium salts.

The looked for improvement, as previously indicated (1), must be presumed to consist either of the removal (or the chemical blocking) of the carboxyl group which is an inherent, terminal part of the protamine molecule, of the removal of acidic impurities contained in the commercial preparations, or of a combination of the two. If the presence of some acidic impurities in the protaminic preparations used is the cause of the deficient ionic selectivity of the membranes, the solution of the problem could be expected from a thorough purification of the protamine preparations.

Preliminary experiments with the commercial protamine preparations available at present regularly yielded membranes of higher ionic selectivity than those described previously, with considerable differences according to the particular batch of protamine used. Different samples of protamine were found to be of different purity as evidenced also by differences in color, from pure white to distinctly yellow, the least yellowish preparations generally yielding the best membranes. This observation also agrees with the results of earlier attempts to purify protamine in which the repeated dissolution and reprecipitation of commercial protamine preparations had led in some instances, but not in a satisfactorily reproducible manner, to membranes of greatly increased anionic selectivity (15).

Thus, the thorough purification of protamine was the obvious initial step in our attempt to improve the ionic selectivity of protamine collodion matrix membranes.

## Preparation of Improved Permselective Protamine Collodion Matrix Membranes

A consistently successful method of purifying protamine to a degree adequate for our purpose is the following: Fifty grams of commercial protamine sulfate is extracted repeatedly with ethyl ether until a sample of the ether on evaporation does not leave any trace of residue. (With preparations already free of lipid-like ether soluble contaminants this step may be omitted.) The ether-wet protamine sulfate is dried, and a nearly saturated, approximately 6.5% aqueous solution is prepared (which in all instances proved to be very close to neutral). To remove all impurities of an acidic (anionic) character from this solution, it was passed through a column consisting of 1 kg of strong base anion exchange resin (Amberlite IRA -400) in the chloride form. While the protamine solution is run slowly through the column, the eluate is continuously tested with trichloroacetic acid and discarded until a positive test, a white precipitate, is obtained. After the last of the protamine solution has been run on the column, the column is slowly washed with distilled water and the eluate collected until it no longer gives a positive reaction with trichloroacetic acid. The solution containing the protamine (now in the chloride form) may either be diluted appropriately and used directly in the preparation of membranes, or dry protamine chloride may be obtained as a fine white powder by the conventional method of freezing and drying *in vacuo*. It might be added that this purified protamine chloride when reconverted to protamine sulfate on an ion exchange column yielded membranes which are significantly inferior in ionic selectivity to those prepared with the purified protamine in the chloride state.

The preparation of permselective membranes consists of casting collodion membranes of high porosity, followed by adsorption on the membranes of protamine from aqueous solutions, and controlled drying (1, 2). Three-layer membranes were prepared routinely at room temperature and at relative humidities between 20% and 50% from a 4.0%solution of Parlodion (Mallinckrodt) in 50:50 etheralcohol containing 2% water. This solution was poured over 25 x 100 mm test tubes rotating in the horizontal position. Ordinarily, the first layer was dried 3.0 min, and the second 3.5 min; 4.0 min after the third laver was poured the membranes were immersed in water. When membranes of higher resistance were desired, these drying periods were each extended by 30 sec. After being washed for an hour in several changes of water, the membranes were slipped off their casting tubes and washed for 3 to 4 hr. They were then immersed in a solution containing 10 g of protamine chloride per liter, buffered to a pH of about 10.5 with a sodium hydroxide-sodium borate-sodium chloride buffer (0.05N NaOH, 0.05N Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O, 0.375N NaCl).<sup>3</sup> The membranes were kept in this solution for periods ranging from 12 to 48 hr depending on the resistance desired, shorter immersion times yielding membranes of higher resistance. Thereafter the membranes were washed for 5 min in distilled water, replaced on their casting tubes, and dried for 24 hr in a humidistat over saturated CaCl<sub>2</sub> solution, at a relative humidity of 31%. Next, the membranes were placed in water for 2 hr, removed from their casting tubes, and tied with linen thread to glass rings fitted into their open ends. They were again dried for 24 hr at 31% relative humidity and then placed in 0.1N KCl solution. After an aging period of several days in this solution, their properties are virtually constant. These test tube shaped membranes were about 30-40  $\mu$  thick, transparent, glass clear, and smooth.

The permselective membranes prepared with the purified protamine preparations, like the earlier types of protamine collodion matrix membranes, are very stable. They do not show any significant deterioration either in ionic selectivity or in mechanical strength over periods of a few years when stored in 0.1N KCl solution to which a preservative such as thymol was added for protection against mold growth. With respect to stability the protamine collodion matrix membranes are superior to the poly-2-vinyl-N-methylpyridinium collodion matrix

 $<sup>^{\</sup>rm 3}$  These solutions of protamine could be used repeatedly with adjustment of pH as necessary. They were stored routinely in a refrigerator to prevent bacterial growth and other forms of deterioration.

1 Time of im- mersion in 1%	2 Anion- exchange	3 Anion- exchange canacity	4 Water content	5 Rate of osmotic water movement (0.2M sucrose)		7 Av. concn. potential 0.4N KCl   0.2N KCl
chloride, hr	meq/g	$\mu eq/cm^2$	%	mm <sup>3</sup> /hr 100 cm	ohm-cm <sup>2</sup>	$(t = 25.00^{\circ}), mv$
12ª	0.141	0.76	7.6	15.0	4500 (1620)	-15.32 (0.08)
24ª	0.163	0.99	8.5	16.0	2130 (780)	-15.66 (0.05)
80	0.229	1.36	9.6	22.0	660 (310)	-15.62 (0.06)
52ª	0.304	1.91	12.7	36.0	189 (66)	-15.43 (0.06)
16%	0.359	2.43	22.1	88.0	45.0 (9.0)	-15.22(0.13)
32°	0.410	2.59	22.2	255.0	17.7 (8.5)	-15.18 (0.18)

Table I. Properties and functional behavior of various permselective protamine collodion matrix membranes

 $^a$  Drying times of 3.5, 4.0, and 4.5 min.  $^b$  Drying times of 3.0, 3.5, and 4.0 min.  $^c$  Figures in parentheses indicate maximum deviation from mean value.

membranes, some of which become very brittle in a period of two months.

## **Properties of Improved Protamine Collodion** Matrix Membranes

For a series of survey experiments, six different sets of twelve membranes each were prepared under carefully controlled conditions and characterized by (a) anion-exchange capacity, (b) water content, (c) rate of osmotic water movement, (d) ohmic resistance in contact with 0.1N KCl solution, and (e) concentration potential in the cell 0.4N KCl membrane 0.2N KCl (see Table I).

Following the survey, membranes of the types most useful for physicochemical investigations were studied for their electromotive properties in KCl concentration cells over a wide range of concentrations, the concentration ratio being 2:1 (see Table II). One of these membranes was tested similarly in analogous cells with HCl, KNO<sub>3</sub>, KIO<sub>3</sub>, and K-Acetate (see Table III). The rates of exchange of critical ions (anions) and of noncritical ions (cations) across representative membranes at three concentrations, 1.0N, 0.1N, and 0.01N, were determined as a measure of their absolute permeabilities and ionic selectivities, and the corresponding ratios, the ionic selectivities of the membranes, calculated (see Table IV). In addition the bi-ionic potentials across several representative membranes were measured with various pairs of critical ions.

The anion-exchange capacity was determined with three or four membranes selected at random from each of the six sets. The membranes were slit open lengthwise, and 5.0 x 7.0 cm rectangles cut from the flat portions were placed in 0.1N KCl solutions which were changed several times during a week to assure that all accessible fixed charged groups were in the chloride form. The membranes were then washed with distilled water for several days until chloride could not be detected in the wash water. The chloride ions in the membranes were then displaced by immersing each group of three or four membranes in 20 ml of 0.5N NaNO<sub>3</sub> solution. After standing three days with occasional stirring, the NaNO<sub>s</sub> solutions were analyzed for chloride ion and the anion-exchange capacities of the membranes in  $\mu eq/cm^2$  calculated. The dry weights of the membranes (see below) were used to calculate the anion-exchange capacities per gram of dry membrane.

The water content was measured with the flat membranes used in the anion-exchange measurements. They were reconverted to the chloride form, washed, blotted dry with filter paper, placed immediately in tared weighing bottles, and weighed in the wet state. They were then dried over phosphorus pentoxide in vacuo. The loss in weight was taken as the water content. The reproducibility of the measurements was about  $\pm 0.5$  g, when the results are expressed as g water/100 g wet membrane

The rate of osmotic water movement across a membrane was measured by filling the test tube shaped membrane with a 0.2M solution of sucrose (for which they are virtually impermeable), fitting it with a rubber stopper carrying a graduated capillary manometer tube, and placing it in a beaker of water at  $25^{\circ} \pm 0.05^{\circ}$ . After thermal equilibrium was reached, the rise of the liquid in the capillary gave

Table II. Concentration dependence of the concentration potentials (c1:c2 = 2:1) with solutions of KCI across representative permselective protamine collodion matrix membranes of different resistance ( $t=25.00^\circ\pm0.05^\circ$ )

$\rho^{\bullet} = 49.5$ ohm-cm <sup>2</sup> , mv	$\rho^* = 188$ ohm-cm <sup>2</sup> , mv	$\rho^* = 660$ ohm-cm <sup>2</sup> , mv	$ ho^*=2300$ ohm-cm <sup>2</sup> , mv
-17.28	-17.30	-17.31	-17.31
-17.19	-17.20	-17.20	-17.18
-17.10	-17.10	-17.10	-17.10
-16.83	-16.84	-16.84	-16.83
-16.54	-16.55	-16.56	-16.55
	-16.18	-16.19	-16.18
-15.85	-15.88	-15.91	-15.91
-15.33	-15.40	-15.64	-15.67
-14.54	-14.92	-14.93	-14.86
-13.33	-13.63	-14.08	-14.25
	$\begin{array}{r} \rho^{\bullet} = 49.5\\ \text{ohm-cm}^2, \text{mv} \end{array} \\ \hline \\ -17.28\\ -17.19\\ -17.10\\ -16.83\\ -16.54\\ -16.54\\ -16.16\\ -15.85\\ -15.33\\ -14.54\\ -13.33 \end{array}$	$\begin{array}{c cccc} p^{*} = 49.5 & p^{*} = 188 \\ \hline & ohm-cm^{2}, mv & ohm-cm^{2}, mv \\ \hline & & & \\ \hline & & & \\ \hline & & & \\ -17.28 & -17.30 \\ -17.10 & -17.20 \\ -17.10 & -17.20 \\ -16.83 & -16.84 \\ -16.54 & -16.55 \\ -16.16 & -16.18 \\ -15.85 & -15.88 \\ -15.33 & -15.40 \\ -14.54 & -14.92 \\ -13.33 & -13.63 \\ \end{array}$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

Table III. Concentration potentials (c<sub>1</sub>:c<sub>2</sub> = 2:1) of several electrolytes across a permselective protamine collodion matrix membrane ( $\rho^* = 660$  ohm-cm<sup>2</sup>) (t = 25.00° ± 0.05°C)

of electrolyte solutions c1/c2	Concentra Theoretical maximum E <sub>max</sub> .	tion potential Experimental (corrected) E <sub>exp</sub> .	Diffusion $E_1$ , in fre $E_1(calc.)$	potential e solution El(exp.
	A. Pot	assium iodate		
equiv/liter	mv	mv	mv	mv
0.002/0.001	-17.5	-17.0	5.5	5.0
0.004/0.002	-17.3	-16.8	5.5	5.0
0.010/0.005	-16.9	-16.8	5.4	5.0
0.020/0.010	-16.7	-16.6	5.3	5.1
0.040/0.020	-16.1	-16.0	5.2	5.0
0.100/0.050	-15.1	-14.9	5.0	49
0 200/0 100	-14.1	-13.8	4.8	47
0.400/0.200	_			
	B. Pot	assium nitrate		
equiv/liter	mv	mv	mv	mv
0.002/0.001	-17.52	-16.98	0.27	0.27
0.004/0.002	-17.40	-16.92	0.27	0.32
0.010/0.005	-17.12	-16.76	0.28	0.38
0.020/0.010	-16.72	-16.50	0.29	0.46
0.040/0.020	-16.27	-16.12	0.29	0.54
0.100/0.050	-15.58	-15.26	0.31	0.64
0.200/0.100	-15.02	-14.92	0.34	0.85
0.400/0.200	-14.19	-13.95	0.39	1.00
	C. Pota	ssium acetate		
equiv/liter	mv	mv	mv	mv
0.002/0.001	-17.43	-17.02	5.07	5.15
0.004/0.002	-17.34	-17.13	5.09	5.06
0.010/0.005	-17.16	-16.94	5.11	4.84
0.020/0.010	-16.97	-16.85	5.11	4.56
0.040/0.020	-16.82	-16.77	5.18	4.23
0.100/0.050	-16.79	-16.63	5.35	4.08
200/0.100	-16.85	-16.55	5 50	3.95
.400/0.200	-17.27	-16.20	5.82	3.86
	D. Hyd	rochloric acid		
equiv/liter	mv	mv		
0.002/0.001	-17.45	-17.30	Concen	tration
0.004/0.002	-17.34	-17.09	potentia	als were
.010/0.005	-17.15	-17.12	measur	ed with
.020/0.010	-16.97	-16.93	Ag/Ag(	Cl elec-
.040/0.020	-16.84	-16.70	trodes;	see text
.100/0.050	-16.76	-16.43		
· · · · · · · · · · · · · · · · · · ·	-16.87	-15.60		
.200/0.100				

The ohmic resistance of the membranes in 0.1N KCl solution,  $\rho^*$ , was measured at  $25^\circ \pm 0.05^\circ$  using the Kohlrausch method as previously described (16). From the measured resistance and the known free area of the membrane (about 50 cm<sup>2</sup>) the unit area resistance was computed.<sup>4</sup> The reproducibility of the

membrane resistance from day to day was about  $\pm 3\%$ .

The concentration potentials of the membranes were measured at  $25^{\circ} \pm 0.05^{\circ}$  using saturated calomel half-cells with saturated potassium chlorideagar bridges, except in the case of the HCl-cells in which Ag AgCl electrodes, prepared by the method of Rule and La Mer, were used (17). Stirring had no effect at any concentration with membranes of  $\rho^*$  of several hundred ohm-cm<sup>2</sup> and more. With membranes having a  $\rho^*$  of about 100 ohm-cm<sup>2</sup>, stirring was necessary at concentrations below about 0.2N/0.1N; otherwise, particularly at the lowest concentrations, the potentials were up to 0.5 my too low. The majority of the potential measurements were reproducible within  $\pm 0.05$  mv except with the highest and lowest concentrations used, where the error may be twice as large.

From these raw data the true concentration potentials were obtained by the following two procedures. Where Ag/AgCl electrodes were used the difference of the two electrode potentials was computed from the Nernst equation using the known mean activities of the pairs of KCl solutions under consideration, and subtracting this computed value from the experimentally determined potential. In the case of the cells with which calomel half-cells and saturated KCl-agar bridges were used for the potential measurements, the corrections for the asymmetry of the two liquid-junction potentials, potassium chloride-agar bridge electrolyte c, electrolyte c<sub>2</sub> potassium chloride-agar bridge, were determined by the following method which had also been used on prior occasions (4, 18). It is based on the assumption that it is possible to calculate with considerable accuracy (from the Nernst equation and known ionic mobility data) the liquid-junction potentials,  $E_{1(calc.)}$ , arising between solutions of the same electrolyte at different concentrations. These calculated liquid-junction potentials,  $E_{1(cale.)}$  are compared with the experimental liquid-junction potentials,  $E_{1(exp.)}$ , in the membrane-free cells: saturated calomel electrode saturated potassium chloride saturated potassium chloride-agar bridge electrolyte  $c_2$  electrolyte  $c_1$  saturated potassium chloride-agar bridge | saturated potassium chloride | saturated calomel electrode. The difference between these two values,  $E_{1(calc.)} - E_{1(exp.)}$ , is taken as the value of the asymmetry of two liquid-junction potentials at the tips of the agar bridges; it is applied as a correction to the concentration potentials measured across the membrane.

The values of  $E_{1(\exp,)}$  were measured with a simple W-shaped tube with a glass stopcock in the middle; otherwise the instruments used and the technique employed were the same as were used for the determination of the concentration potentials across membranes. The reproducibility of the  $E_{1(\exp,)}$  data, except at the lowest concentrations used, is better than  $\pm 0.05$  mv. The various values for  $E_{1(\exp,)}$  and  $E_{1(\exp,)}$  are given in Table III for the neutral salts except KCl. With KCl cells with a concentration is -0.33 mv independent of the concentration. All data

<sup>&</sup>lt;sup>4</sup> Dimensionally this resistance in ohm-cm<sup>3</sup>, the reciprocal of the unit area conductance which is expressed in moh/cm<sup>2</sup>. The designation of the unit resistance as ohm/cm<sup>2</sup> which is common in the literature (including some older publications from this laboratory) is dimensionally in error.

Table IV. Rates of movement of critical and noncritical ions across several permselective protamine collodion matrix membranes at various concentration levels in the system KCI (c1) || NH4CI (c1)

1	2	3 0.1N	4	5	6 Concentration 0.1N	7	. 8	9 0.01 <i>N</i>	10
Membrane $\rho^*$ , ohm-cm <sup>2</sup>	Initial rate of movement of Cl- µeq/hr cm <sup>2</sup>	Initial rate of movement of NH4 <sup>+</sup> µeq/hr cm <sup>2</sup>	Ratio of initial rates of movement of Cl- to NH4+	Initial rate of movement of Cl- µeq/hr cm <sup>2</sup>	Initial rate of movement of NH4+ µeq/hr cm <sup>2</sup>	Ratio of initial rates of movement of Cl- to NH4+	Initial rate of movement of Cl- µeq/hr cm <sup>2</sup>	Initial rate of movement of NH <sub>4</sub> + µeq/hr cm <sup>2</sup>	Ratio of initial rates of movement of Cl- to NH4+
5040	0.366	0.025	14.6	0.192	$7.8 imes10^{-4}$	250	0.180	$5.8 imes10^{-5}$	3100
2780	0.638	0.034	18.7	0.376	$1.1  imes 10^{-3}$	340	0.304	$4.6 \times 10^{-5}$	6600
450	4.64	0.380	12.2	2.46	$5.6 \times 10^{-3}$	450	1.71	$2.00 \times 10^{-4}$	8550
113	17.9	1.09	16.4	8.34	$2.10 \times 10^{-2}$	400	5.56	$4.6 \times 10^{-4}$	12000
24.5	121	16.7	7.2	42.8	$2.69 \times 10^{-1}$	160	15.0	$6.5 \times 10^{-3}$	2300
9.5	267	33.6	7.9	110	1.18	93	17.2	$1.36 imes10^{-2}$	1250

on membrane concentration potentials given in this paper are appropriately corrected.

The thermodynamically possible maximum values of the concentration potential were calculated in the conventional manner assuming that the only process occurring across an ideal membrane is the reversible transfer of the critical ions from the one solution to the other, and that the activity of the critical ions, the anions, at any given concentration is equal to the mean activity of the electrolyte  $(a_{-} = a_{1})$ . The activity coefficients were taken from Harned and Owen and from Robinson and Stokes, and converted from the molality to a normality basis (19, 20).

For the measurement of the rate of exchange of the anions a membrane filled with a KCl solution containing radioactive  $Cl^{ss}$  was placed in a large volume of solution of nonradioactive KCl of the same concentration. Both solutions were stirred. Aliquots of the outer solution were withdrawn periodically and their radioactivity determined. The initial rate of anion exchange was calculated from the fraction of the radioactive chloride exchanging for stable chloride per unit time.<sup>5</sup>

The strictly comparable initial rate of exchange of the cations can be obtained from analogous experiments only with membranes of very low resistance and a significant leak because of the short half life  $(t_{1/2} = 12.4 \text{ hr})$  of the available potassium isotope K<sup>42</sup>. Instead, with the membranes of the extremely low cation leak of particular interest here, the rate of exchange of cations between an NH<sub>4</sub>Cl and a KCl solution of equal concentration was determined by conventional microanalysis. The use of the data for these rates instead of those for the self-exchange of K<sup>+</sup> seems unobjectionable for the present purpose for the following reasons: (a) the behavior of  $NH_4^+$ and K<sup>+</sup> ions in solution is very similar, and likewise, with cation selective membranes, as is evident from the fact that the bi-ionic potential, NH4+ cation selective permselective membrane | K<sup>+</sup> is very low, at best of the order of a few millivolts; (b) the rates of exchange  $K^{39+} \leftrightarrows K^{42+}$  and  $NH_4^+ \rightleftarrows K^+$  across permselective poly-2-vinyl-N-methylpyridinium collodion matrix membranes have been found to agree satisfactorily in the case of those membranes with which both rates could be determined (14).

In addition, a few analogous experiments on the rates of exchange of critical and noncritical ions were carried out with CaCl<sub>2</sub> solutions in which the rates of exchange of the bivalent noncritical Ca<sup>++</sup> ions were obtained by the use of Ca<sup>+5</sup> ( $t_{1/2} = 152$  days).

The bi-ionic potential in cells of the type 0.1N KCl | membrane | 0.1N KX where X may be any anion other than chloride, was measured (with all the precautions described recently elsewhere), using saturated calomel half-cells with saturated potassium chloride-agar bridges (21). The measurements were reproducible in general within  $\pm 0.5$  mv. No corrections were made for the asymmetry of the liquid junction potentials at the tips of the two agar bridges.

### Discussion

The exchange capacity per gram of membrane (Table I, column 2) is of interest primarily in correlation to certain aspects of the Teorell, Meyer-Sievers theory of the electrochemical behavior of membranes. This point will be touched upon later.

The exchange capacity per square centimeter of the membranes (Table I, column 3) is low, of the order of 1 to 2.5  $\mu$ eq/cm<sup>2</sup> with the most useful of these membranes. Thus, in many types of experiments, it is possible to use membranes whose exchange capacities are low relative to the number of equivalents of ionic constituents in the surrounding solutions. This is of importance in many physicochemical investigations such as, for example, in the electrometric determination of ionic activities and in the study of Donnan equilibria.

The water content of the membranes (Table I, column 4) is the higher the longer the time of immersion of the membranes in the protamine solution and the less dried, that is, the more porous the membranes were during this immersion.

The rate of osmotic water movement across the membranes (Table I, column 5) is greater the higher the water content (cf. col. 4). The water movement across the membranes which is measured under a driving force corresponding to 50 m of water pressure is low except in the case of those with the highest protamine content. The low water permeabilities are helpful in studies where it is necessary to keep solutions of different water ac-tivity separate for long periods.

The resistances (Table I, column 6) of the membranes of a given type prepared under nominally identical conditions show substantial variations. Small increments in anion-exchange capacity are accompanied by great differences in resistance.

<sup>&</sup>lt;sup>5</sup> A detailed account of the experimental technique is planned for a forthcoming paper on the exchange of ions across permselective membranes by Gottlieb and Soliher, in preparation (14).

The degree to which the concentration potentials (Table I, column 7) of the membranes deviate from the theoretical maximum at the 0.4/0.2N KCl concentration level can be estimated by comparing them with the calculated theoretical maximum potential, -15.95 mv.

The concentration potentials across the membranes with medium protamine contents approach the maximum theoretical potential more closely than do those with very low or very high protamine contents. The lower concentration potential obtained with the membrane with the lowest protamine contents is very probably due to the absence of charged groups at critical points in some of the pores of these membranes. With membranes of high protamine content the lower concentration potentials are undoubtedly due to the larger average pore size of these membranes which is correlated with their higher water content (cf. col. 4).

In connection with the Teorell, Meyer-Sievers theory (22, 23) it is of interest to look for a correlation of the selectivities of the various membranes as manifested by their concentration potentials and the equivalent concentrations of fixed basic wall groups (or exchangeable counter ions) in the pore water of the membranes. The latter values as derived from col. 3 and 4 of Table I, assuming all of the water to be available, are in order of increasing anion exchange capacity per gram of wet membrane, 1.7, 1.8, 2.2, 2.1, 1.3, and 1.4 equiv/1. These values are identical with the selectivity constants of the Teorell, Meyer-Sievers theory. The theory postulates the concentration potentials to be the higher the greater the equivalent concentration of active groups in the pore water of the membrane. The empirically found correlation is more of a general qualitative than of a quantitative nature.

Table II on the concentration dependence of the concentration potential in KCl cells shows that the potentials at the lowest concentrations are 0.15 - 0.28 mv below the calculated maximum; at 0.01/0.005N and 0.02/0.01N the agreement is perfect within the accuracy of the measurements, except possibly with the membrane of lowest resistance. With more concentrated solutions the deviations become greater. The electromotive behavior of the permselective protamine membranes in this series of concentration cells is virtually the same as that of the analogous strong-base type poly-2-vinyl-N-methylpyridinium bromide collodion matrix membranes (13).

Table III gives the calculated and the (corrected) experimental concentration potentials in cells with four different electrolytes, KIO<sub>s</sub>, KNO<sub>s</sub>, K-Acetate, and HCl, together with the calculated and experimental liquid junction potentials obtained with the three neutral electrolytes (on which the corrections of the measured potential values are based). In all instances, as above with the KCl cells, the agreement between the theoretical and experimental concentration potentials is best in a medium range of concentrations.

In order to facilitate visualization of the data on concentration potentials a part of the data of Table



Fig. 1. Concentration potentials ( $c_1$ : $c_2 = 2$ :1) of several electrolytes across typical permselective protamine collodion matrix membranes.

II and the data of Table III are represented graphically in Fig. 1. The deviations of the experimental values from the calculated ones at the higher concentrations do not require any comment: it is in full agreement with the fixed charge theory (22, 23). Deviations between the two sets of data at the lower and particularly the lowest concentrations, which are quite systematic and, with the neutral salts, far in excess of any probable error, are not explained by the fixed charge theory as commonly understood. They duplicate earlier observations with the older type of permselective protamine collodion matrix membrane (4) and with poly-2-vinyl-N-methylpyridinium collodion matrix membranes (13). Analogous deviations at the lowest concentrations were also observed with strong acid sulfonated polystyrene collodion membranes (24). We are inclined to attribute this effect to the ions of the water, specifically to the drift of the experimental cells toward the state of membrane hydrolysis predicted by the theory of membrane equilibria. Preliminary experiments support this view, without as yet definitely proving its correctness. We hope to report on this matter in the near future.

It was recognized some time ago that the deviations of the measured concentration potentials from the theoretically possible maximum values, particularly in the case of membranes of high ionic selectivity, do not furnish an adequate basis for a calculation of the numerical value of the ionic selectivities of such membranes (25). A variety of complicating factors is now generally recognized (26).

First, nonthermodynamic assumptions are made in the calculation of the theoretical maximum potential; and, likewise, in assigning a part of the measured potential of a concentration cell to the membrane concentration potential a nonthermody-

namic, at least semi-empirical correction procedure must be used, such as that outlined above. Second, there are definite limitations of the accuracy with which the potential measurements may be made. In particular, if a membrane is not of virtually ideal ionic selectivity and if the solutions are very dilute, the concentrations of electrolyte in the nonstirred, adhering water layers of the membrane may be significantly different from those in the bulk solutions. The measured potential would thus be lower than that which would arise if the concentrations in the adhering water layers and bulk solutions were the same. Expressed in another way, the true ionic selectivity of the membrane would be higher than that calculated in a straightforward manner from the measured concentration potential. Further, membrane hydrolysis may also lower the measured potential in dilute solutions of neutral electrolytes. In addition, the ions move across the membranes in a hydrated state, thereby transporting water of hydration from a compartment of lower to the compartment of higher water activity (and possibly some additional water by an electrophoretic effect). There may also be an opposing osmotic streaming of water which the diffusing critical ions must overcome. All these effects would tend to reduce the electromotive efficiency of the critical ions, thus reducing the concentration potential below the value which is calculated for the condition of no solvent transport between the two solutions. These latter possibilities, in recent years, have been the subject of intensive theoretical and experimental work (21, 26-29). Thus it is apparent that the degree of the ionic selectivity of highly ion selective membranes is better established by a more direct method, namely, on the basis of the relative permeabilities of the critical and noncritical ions as determined from the rates of self-exchange of these ions across a membrane (13, 14, 24, 25).

The initial rates of movement of critical ions, the anions, across the various membranes in the systems at 0.1N (Table IV, column 5) are inversely proportional to their standard resistances,  $\rho^*$ , (which is also measured with 0.1N solution) as postulated by the Nernst-Einstein equation for the rate of selfdiffusion. With 1N and 0.01N solutions (columns 2 and 8 of Table IV) the rates of self-exchange of the critical ions show only a semi-quantitative inverse proportionality to the standard resistance of the membranes,  $\rho^*$ .

The initial rate of movement of the noncritical ions, the cations, (columns 3, 6, and 9 of Table IV) shows a considerably steeper inverse relationship with the standard membrane resistance than that observed with the critical ions.

The rates of exchange of the critical ions across a given membrane in 0.01 and 1N solutions differ by a factor of about 2 with the membrane of the highest standard resistance to a factor of about 15 with the membrane of lowest resistance. The rate of exchange of the noncritical ions varies over the same concentration interval by a factor of about 430 for the membrane with the highest resistance, to a factor of about 2500 for the lowest resistance membrane.

The ionic selectivities of the various permselective membranes, that is, the ratio of the initial rates of exchange of the critical to those of the noncritical ions (columns 4, 7, and 10 of Table IV) are very much greater at the lower than at the higher concentrations, in agreement with all previous experience.

The correlation between membrane resistance and selectivity is not straightforward; the best membrane with a selectivity of 12,000:1 in 0.01N KCl solution is of medium resistance. The degree of ionic selectivity of the permselective protamine collodion matrix membranes closely approaches, but does not quite reach, that of the analogous permselective poly-2-vinyl-N-methylpyridinium collodion matrix membranes (13).

The small "leaks" of noncritical ions which correspond to these high ionic selectivities (numerically their reciprocals) circumscribe the conditions under which these membranes can be used without significant disturbances due to this imperfection.

The selectivities of the improved permselective protamine collodion matrix membranes, in the presence of univalent anions and bivalent cations (not shown in the tables) as determined with  $0.1N \text{ CaCl}_2$  solutions containing radioactive Ca<sup>45</sup>, and membranes of 10, 23, 108, and 402 ohm-cm<sup>2</sup> in 0.1N KCl were found to be 10.400, 15.000, 48.000, and 151.000 ohm-cm<sup>2</sup>, respectively. With more dilute solutions these selectivities can be safely assumed to be considerably higher.

The bi-ionic potentials across the permselective collodion matrix membranes prepared with purified protamine preparations, as may be expected *a priori*, are very similar in magnitude to those obtained earlier with membranes made with less pure preparations (30). Some of the bi-ionic potentials,  $E_{\rm styp}$ , obtained (with 0.1N solutions) across a membrane with a standard resistance,  $\rho^*$ , of 660 ohm-cm<sup>2</sup> were: NaCl || NaSCN, + 31.4 mv; NaCl || NaNO<sub>3</sub>, + 21.1 mv; NaCl || NaI, + 16.3; NaCl || NIO<sub>3</sub>, - 38.3 mv; NaCl || Na-acetate, - 46.0 mv; and NaCl || Na-propionate, - 52.5 mv, the signs referring to the charge of the solutions on the right side.

The improvement in the ionic selectivity of the membranes prepared with purified protamine over those prepared with the commercial preparations obviously must be ascribed to the removal of some strongly adsorbable impurities of acidic character which are removed by the treatment with the ion exchange resin since it can hardly be assumed that the treatment with an ion-exchange column alters the chemical structure of protamine itself. As is evident from the data, the carboxylic end groups of the protamine molecules do not affect adversely the ionic selectivity of the membranes to any significant extent, in spite of the fact that they represent about 5% of the potentially dissociable groups of the protamine molecule.

Several factors should be considered to account for the functional ineffectiveness in the membrane of the carboxylic end groups of the protamine molecule. First, many of these groups may be blocked functionally by combination with a basic group

either of the same or of some other protamine molecule. Second, the cationic counterions of the sparsely distributed acidic groups, even if dissociated completely off the latter." would have to migrate past numerous interposed positive wall groups. Being strongly repelled by these groups of the same charge, the cations are unable to move from the vicinity of one of the acidic groups to the next and thus are more or less permanently confined to the location which they had occupied when the membrane was prepared.

The high ionic selectivities of the improved protamine collodion matrix membrane which are evident from Tables I-IV demonstrate that the purpose of this investigation has been achieved, namely, to produce membranes which are free of the main shortcoming of the previous protamine membranes, their inadequate degree of ionic selectivity, and which fulfill the predictions of the Nernst-Einstein equation with respect to the correlation of their resistance and the rate of self-exchange of ions across them.

<sup>6</sup> Due to the mode of preparation of the membranes, the carboxyl groups may be present in the hydrogen state with the hydrogen ion dissociated off to a very limited degree only.

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# **December 1959 Discussion Section**

A Discussion Section, covering papers published in the January-June 1959 JOURNALS, is scheduled for publication in the December 1959 issue. Any discussion which did not reach the Editor in time for inclusion in the June 1959 Discussion Section will be included in the December 1959 issue.

Those who plan to contribute remarks for this Discussion Section should submit their comments or guestions in triplicate to the Managing Editor of the JOURNAL, 1860 Broadway, New York 23, N. Y. not later than September 1, 1959. All discussions will be forwarded to the author(s) for reply before being printed in the JOURNAL.

# **Electrochemical Kinetics of the Anodic Formation of Oxide Films**

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### ABSTRACT

The total electric potential difference between a metal and a solution across an oxide film being built up by a constant anodic current is decomposed into three contributions: differences at the interphases metal-oxide and oxide-solution, both subject to activation overvoltage, and the difference across the oxide layer. For one or the other of the interphases the case of linearity of overvoltage with the logarithm of the current (in the range of large currents) and that of proportionality of overvoltage with current (in the range of small currents) are examined in some detail, and previously obtained experimental data for three types of titanium, for hafnium, and for tantalum are analyzed in terms of the proposed theoretical treatment. Numerical values are obtained for the various parameters appearing in the equations: thickness of the interphase, exchange current, electric potential difference, and electric field at zero current. Possibilities for refinement and extension of the treatment are mentioned.

The theory advanced by Cabrera and Mott (1) on the basis of earlier work by Mott (2) to explain the rate of growth of oxide films on metals usually has been regarded as directly applicable to the case of anodic oxidation. The present authors and their collaborators (3-5) have applied it to the interpretation of data obtained in the anodic oxidation of several metals. From the evolution with time of the potential of the metal (measured against an unpolarized electrode) during oxidation at constant current they were able to verify that the unitary rate of change of potential,  $(1/I) \cdot (\partial E/\partial t)_I$ , in which I is the apparent current density, E the relative potential of the metal, t the time, corresponding to the flats in the curves  $\log(\partial E/\partial t)_1$  vs. log t at constant I was, over the range of currents utilized (1 to 100  $\mu a/cm^2$ ), a linear function of log I. This situation is implied in the Cabrera-Mott theory which thus was regarded as essentially verified.

In a more detailed analysis of our recently published data (5) on the anodic oxidation of Al, Cr, Hf, Nb, Ta, Ti, and V in saturated ammonium borate at 25°C, it was found interesting to interpret these data on the basis of an electrochemical approach involving the use of the current-overvoltage relationships of electrochemical kinetics at the metal-oxide and at the oxide-solution interphase. Regardless of the detailed circumstances of the passage of the current through the oxide film itself, it appears probable that, at the metal-oxide interphase, the net process is the transfer of metallic ions from the metal to the oxide and that, at the oxide-solution interphase, the net process is the transfer of oxide or hydroxyl ions from the solution to the oxide. The treatment presented here does not depend on an a priori decision as to which process (that across the metal-oxide interphase, that across the oxide itself,

or that across the oxide-solution interphase) is ratedetermining. In a steady state, with the same current passing through the three portions of the overall metal-solution system, the evaluation of the velocity of one of the three processes serves for the two other processes as well. This has been the guiding idea of one of us in previous treatments of overvoltage phenomena (6).

Following Cabrera and Mott (1) and Vermilyea (7) we shall neglect the possibility of the presence of a space charge anywhere in the over-all interphase, the electric field being then constant from the bulk of the metal to the bulk of the solution.

#### Electrochemical Theory of Anodic Oxidation

Consider a metallic phase  $\alpha$  separated from an electrolyte solution  $\beta$  by a film  $\gamma$  of oxide (Fig. 1). Between the terminal plane a' of the metal and the oxide in bulk there is a transition layer a'a and between the oxide in bulk and the solution in bulk there is a transition layer bb'. The oxide has the thickness X from a to b. The thicknesses a'a and bb' are called  $x_a$  and  $x_b$ , respectively, and will be regarded as independent of time. We shall restrict ourselves to values of X large enough to prevent any overlapping or mutual influence of the transition



Fig. 1. Model used for metal-oxide-solution system

regions a'a and bb' but small enough to remain in the range of thin films.

The electric potential difference from metal to solution is given by

$$\phi_a - \phi_\beta = (x_a + x_b + X) \cdot F \qquad [1]$$

in which F represents the electric field. Calling w the mass of oxide formed per coulomb and d the density of the oxide we have

$$X = X_o + wIt/d$$
 [2]

In electrochemical terms the situation at the a'a interphase can be described as follows. It should be clear that this analysis is equally applicable to the interphase bb'. We shall consider the two extreme cases of: (a) a Tafel relation between current and overvoltage, and (b) proportionality between current and overvoltage. In this latter case, as well as in the intermediate one corresponding to proportionality of current with the hyperbolic sine of  $zF_{\eta}/2RT$  (z being the number of Faradays F carried by one gram-ion,  $\eta$  the overvoltage, R the molar gas constant, and T the absolute temperature; the transfer coefficient is taken as equal to 1/2 for both the anodic and the cathodic direction) the net current is the resultant of a forward anodic current and of a reverse cathodic current. Such a situation may conceivably occur at very low net currents both in a'a and in bb', even though the anodic current through the oxide itself might still be unopposed.

Case 1.-We have the following Tafel relation:

$$(\phi_{\star'}-\phi_{\star})_{I} = (\phi_{\star'}-\phi_{\star})_{I=0} + \frac{RT}{\tau_{\star}zF} \cdot \ln \frac{I}{I_{0\star}} = x_{\star}\cdot F \quad [3]$$

in which  $\tau_a$  is the transfer coefficient (equal to the ratio of distance a'a" to distance a'a in which a" is the activated position of the metallic ion moving across the barrier from a' to a), ln represents the natural logarithm, and  $I_{0a}$  is the extrapolated exchange current at the a'a barrier. Since

$$\phi_{a} - \phi_{\beta} = (x_{a} + x_{b} + X_{0} + wIt/d) \cdot F \qquad [4]$$

we have, combining with Eq. [3] and differentiating with respect to t at constant I, E differing from  $\phi_a - \phi_\beta$  by a constant:

$$\frac{1}{I} \cdot \left(\frac{\partial E}{\partial t}\right)_{I} = \frac{RTw}{\tau_{s} dx_{s} zF} \cdot \ln \frac{I}{I_{\text{os}}} + (\phi_{\text{s}'} - \phi_{\text{s}})_{I=0} \cdot \frac{w}{dx_{s}} = \frac{w}{d} \cdot F$$
[5]

an expression independent of t which thus is expected to be valid only along the horizontal portions of the experimental plots of  $\log(\partial E/\partial t)$ , vs. log t for constant I. This situation is that which we actually verified with several of the metals previously reported on (3-5). Equation [5] was found to apply satisfactorily from current densities of 100  $\mu$ a/cm<sup>2</sup> down to 1. However, plots of unitary rates vs. I rather than vs. log I (8) indicated a definite possibility that the lower current densities, from 5 to 1, might be in or very near the range of applicability of Case 2.

Table I. Data on anodic oxidation of Ti, Hf, and Ta in saturated ammonium borate at 25°C

Metal	Oxide	Density of oxide	xa, A	I <sub>0a</sub> , μa/cm²	(φa'- φa) 0, mv	F ., 10 <sup>6</sup>	<i>F</i> 100, //cm
Ti (iodide)	TiO <sub>2</sub>	4.22	8.7	1.7	205	2.3	3.0
Ti (Kroll)	TiO <sub>2</sub>	4.22	7.1	2.5	176	2.6	3.2
Ti (cold worked)	TiO₂	4.22	7.9	1.1	214	2.5	3.4
Hf	HfO <sub>2</sub>	9.68	8.0	1.5	225	2.8	3.6
Та	Ta <sub>2</sub> O <sub>5</sub>	8.5	6.0	1.7	94	1.6	2.3

Case 2.—When the cathodic counter-current in a'a cannot be neglected the net current is given by a difference between two Tafel expressions which, upon expansion and limitation to first power terms in the overvoltage (a procedure justified when  $r_{u}F\eta/RT$  becomes sufficiently smaller than 1) gives:

$$(\phi_{\mathbf{a}'} - \phi_{\mathbf{a}})_I = (\phi_{\mathbf{a}'} - \phi_{\mathbf{a}})_{I=U} + \frac{RTI}{(\tau_{\mathbf{a}} + \tau'_{\mathbf{a}})zFI_{\mathrm{Oa}}} = x_{\mathbf{a}} \cdot F \quad [6]$$

Instead of Eq. [5] we now have:

$$\frac{1}{I} \cdot \left(\frac{\partial E}{\partial t}\right)_{I} = \frac{RTwI}{(\tau_{a} + \tau'_{a})dx_{a}zFI_{0a}} + (\phi_{a'} - \phi_{a})_{I=0} \cdot \frac{w}{dx_{a}} = \frac{w}{d} \cdot F$$
[7]

an expression which, like Eq. [5], is time-independent and which we may expect to find verified along the horizontal portions of the plots of  $\log(\partial E/\partial t)_{I}$ vs. log t for sufficiently small values of I. Let us note that Eq. [7] leads to the possibility of determining the field at zero current from the intercepts of the linear plots of  $(1/I) \cdot (\partial E/\partial t)$ , vs. I. This is of course not possible with the linear plots of  $(1/I) \cdot (\partial E/\partial t)_I$ vs. log I corresponding to Eq. [5]. However, by combining information obtainable from Eq. [5] and [7] and on the basis of plausible assumptions concerning d,  $\tau_a$ , and  $\tau'_a$  we can arrive at numerical values for all the quantities appearing in these two equations. We have done this for a number of metals by applying Eq. [7] to the range of 5 to  $1 \mu a/cm^2$ , taking the slope provided by these two points to be the coefficient of I in Eq. [7]. In two cases out of five [the first two of Table I, see (8) ] the plots were linear in the range  $1-5-10 \mu a/cm^2$ , while in the other three cases a hyperbolic sine type of behavior appears to hold in the 5-10-20 range.

#### Application to Titanium, Hafnium, and Tantalum

In Eq. [5] and [7] the experimental quantities are the unitary rate  $(1/I) \cdot (\partial E/\partial t)_i$ , the temperature T and the current density I. In addition these equations contain the constants R, w, z, and F. We assume that the density d of each oxide is equal to that of the oxide in bulk, that  $\tau_n$  and  $\tau'_n$  are both equal to 0.5. On this basis it is readily seen that the coefficient of ln I in Eq. [5] immediately will give us the value of  $x_n$ . Introducing this value of  $x_n$  in the coefficient of I in Eq. [7] we obtain the value of  $I_{0n}$ . It is interesting to note, as is shown in Table I, that, in the

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five cases for which these calculations were carried out,  $I_{0a}$  turns out to fall within the 1 to  $5\mu a/cm^2$ range, an indication that this range either corresponds to the exact applicability of the proportionality between current and overvoltage or is one of transition from hyperbolic sine behavior to proportionality. Even if this second alternative were to be the more correct one, it appears to be of extreme interest to pursue the calculations on the basis of proportionality for the 1 to 5 range and thus to obtain from our measured unitary rates at least approximate values for quantities which otherwise would not be accessible: exchange currents, electric potential differences across a'a or bb' interphases and electric fields at I equal to or different from zero.

Another indication in support of our procedure is the following: the term  $(\phi_{a'} - \phi_{a})_{I=0} \cdot (w/dx_{a})$  should have, for internal consistency between Eq. [5] and [7] and their respective ranges of validity, the same value in these two formulas. We verified that this was practically the case by transporting into Eq. [5] the value of  $(\phi_{a'} - \phi_{a})_{I=0} \cdot (w/dx_{a})$  derived from Eq. [7] and calculating the value of  $I_{0a}$  required for verification of Eq. [5]. In the case of hafnium, for instance,  $I_{0a}$  obtained from Eq. [7] is  $1.5 \,\mu a/cm^2$ , while the value obtained from Eq. [5] by the procedure just outlined is 0.9, a very satisfactory agreement in view of the fact that a verification of the order of magnitude was all that had been expected.

The results of the calculations described above are given in Table I for three kinds of titanium (iodide process, Kroll process-annealed, Kroll process-34% cold worked), hafnium, and tantalum. The experimental details concerning these and other metals have been given earlier (5). The formula of the oxide, its density, the thickness  $x_{i}$ , the exchange current  $I_{0a}$ , the electric potential difference ( $\phi_{a'}$  –  $\phi_a$ )  $_{I=0}$ , the field  $F_0$  at zero current and the field  $F_{100}$  at  $I = 100 \ \mu a/cm^2$  are given for each metal.

Our calculations have been carried out without introducing any roughness factor because of the lack of any reliable information concerning its value and also because its theoretical role in the considerations developed here is by no means clear. It may be that the values of  $x_{a}$  empirically obtained in the calculations include an effective roughness factor. Using an arbitrary value of 2, for instance, the actual values of  $x_{*}$  would be those of Table I divided by 2.

Recall that the exchange current  $I_{0a}$  is proportional to exp  $(-\Delta G^*/RT)$  in which  $\Delta G^*$  is the chemical free enthalpy of activation, the electrical portion of the total free enthalpy of activation at zero net current having been separated in the first term on the right hand side of Eq. [3]. The values of  $I_{0a}$  and  $\Delta G^*$  thus vary in opposite directions. It is interesting to note that, of the three kinds of titanium considered here, the Kroll process-annealed has the lowest  $\Delta G^*$  and the Kroll process-cold worked has the highest, with the iodide process type having an intermediate  $\Delta G^*$ , the total range of variation being about 500 cal/gram-ion.

In concluding we wish to stress that the calculations presented here should be regarded as having only qualitative significance. They should serve as illustrations for a theoretical approach which ap-

pears to be in the right direction and which could be refined without any major difficulty. In particular it would be a simple matter to introduce discontinuities in the electric field at the planes a and b and thereby to take into account the possible presence of space charges. The overvoltage-current relationships at the interphases a'a and bb' may each be, for a given current, of one of three possible types (Tafel, hyperbolic sine, proportionality) giving rise to a total of nine possibilities. In accordance with a recent study by one of us (9) on the dependence of reaction rates on affinities, which we are in the process of extending to electrochemical reactions. elementary reactions with rates varying exponentially with their affinities (here currents varying exponentially with the electrochemical affinities or overvoltages) are rate-determining, while elementary reactions with rates proportional to their affinities (here currents proportional to the electrochemical affinities or overvoltages) are regarded as practically reversible steps. If, in the cases discussed above, the current-overvoltage relationship applying to the thickness X of the oxide itself remains of the Tafel (or Cabrera-Mott) type throughout the whole range of currents, i.e., from 100 to  $1 \mu a/cm^2$ , the corresponding step (passage of metallic ions from a to b, but, as a conceivable alternative, passage of oxide ions from b to a) is definitely ratedetermining in the range of small currents, i.e., here 5 to  $1 \mu a/cm^2$ . On the other hand, at the higher currents, the actual rate-determining step may be either the passage of metallic ions from a' to a or the passage of oxide ions from b' to b. In this latter case a variation with the composition of the solution of the parameters calculated in the present paper would be expected. In this manner it would become possible to examine the influence of the composition of the solution on the characteristics of the filmbuilding process. Such an influence has already been detected experimentally in the case of zirconium and its alloys (10, 11).

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## **Electrochemical Aspects of Stress Corrosion**

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In recent years there has been some discussion of a "mechanical" mechanism for stress-corrosion cracking (1-5). In much of this work discussions of mechanism are based on the combination of a mechanical step and an electrochemical step, these being regarded as alternate and discrete actions which contribute to the total phenomenon. Those holding this viewpoint with respect to the mechanism of stress-corrosion believe that purely mechanical cracking is the major contribution toward stresscorrosion cracking and that electrochemical reaction or corrosion acts only as a means of triggering the mechanical cracking.

It is believed that some experimental evidence available indicates another, more logical mechanism for stress-corrosion, and this paper is devoted to discussion of a mechanism for stress-corrosion believed to be in best agreement with observable data.

Harwood, in a review of the phenomenon, discussed several theories of stress-corrosion (6). These theories can be divided into two main areas of belief, a mechanical mechanism, triggered at intervals by very local corrosive attack and an electrochemical mechanism in which corrosive attack occurs continuously as a primary contributing factor with the role of stress being that of causing local electrode potential changes. Such potential changes might be caused by stress-induced changes in filming mechanisms or by cold work of local metal volumes.

Brown and Dix (7) supported an electrochemical mechanism. Their work dealt primarily with intergranular stress corrosion, however, and strong evidence was presented for the existence of preferential paths for corrosion along grain boundaries. Extensions of the electrochemical theory into the area of transgranular stress-corrosion have been made by Logan (8), Priest, Beck, and Fontana (9, 10), among others.

Although the mechanical theory was early expressed by Keating (1), in recent years Edeleanu (4), Harwood (5) and others have held similar although more sophisticated views wherein the electrochemical contribution to stress-corrosion was viewed as a triggering mechanism for a purely mechanical fracture. This expanded viewpoint was made necessary in view of the demonstration of the effectiveness of cathodic protection in preventing stress-corrosion cracking and in slowing or stopping stress-corrosion already in progress.

### Loading Previously Cracked Specimens

Unpublished data and observations recorded by the writer some years ago are of interest in support of the electrochemical theory of stress-corrosion. In an investigation of stress corrosion in a magnesiumbase alloy (9), several interesting experiments were performed. In one case stress-corrosion cracking of the Jl alloy (6% Al, 1% Zn, balance Mg) in an inhibited sodium chloride solution was allowed to proceed until the test specimen was cracked halfway through, at which time it was removed from the test solution, washed and dried, and subjected to additional stress. The imposition of additional stress resulted in no further cracking and caused only ductile bending of the remainder of the cross section. Such cracked specimens could only be cracked further in air by impact loading, in which case the surface appearance of the impact fracture was far different than the surface appearance of the fracture caused by stress-corrosion cracking.

## **Corrosion Current Measurements**

A consideration of the mechanical triggering idea is that measured corrosion currents should assume different values according to whether or not mechanical failure or electrochemical corrosion is taking place within a given time interval. Thus, if purely mechanical cracking is occurring, the corrosion current should be zero or appreciably decreased and, if mechanical cracking is not taking place at the instant of time considered, then corrosion current should assume some maximum value.



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The data presented in Fig. 1 were recorded for a transgranular stress corrosion failure of Jl alloy under testing and measuring conditions described in detail previously (9). The Jl alloy was made to crack in an inhibited sodium chloride solution and, using an electrode physically separated from the anodic crack as cathode, corrosion currents were measured. The data of Fig. 1, recorded at intervals of a minute or less, indicate that the measured currents did not fluctuate and did not increase or decrease in a step-wise manner. Further, continuous visual observation of the microammeter revealed no needle "flicker" or other evidence of changing current. This behavior of the corrosion current suggests that the electrochemical nature of stress-corrosion process is continuous and that purely mechanical cracking plays no role in the mechanism.

#### **Cathodic** Protection

Harwood (5) suggests that at some point in the cracking process, the influence of mechanical cracking might be too great to counteract with cathodic protection. In contrast, the writer's experiments indicate that application of cathodic protection to a specimen undergoing stress-corrosion controlled the *rate* of stress-corrosion at all stages of cracking.

Figure 1 presents typical corrosion current-cracking time data obtained for transgranular stress corrosion cracking with the magnesium-base alloy, Jl. The data cover the total cracking of a specimen from crack initiation to essentially complete failure. Current values were measured as described previously. The shape of the curve in Fig. 1 is due to the fact that the specimens were stressed by the constant deflection method so that stress values at the crack base varied from zero (before initiation) to a maximum (when crack was halfway through the specimen cross section) to zero (as relief occurred because of the ductile behavior of the reduced cross section of the nearly completely cracked specimen). At any stage in the cracking process, the amount of cathodic protection current needed to stop the attack was proportional to the corrosion current being generated at the time of application of protection. Further, at all stages of the process the addition of lesser amounts of cathodic protection current slowed the stress corrosion cracking so that "failure time" was increased.

#### **Corrosion** Rates

Complete cracking of a specimen 3/16 in. thick took place in about 20 min, but the major portion of the cracking occurred in approximately 10 min and, during this time, two-thirds or about  $\frac{1}{2}$  in. of the specimen was cut through. During the fastest cracking period, therefore, a rate of 0.0125 in./min was attained. This is approximately 6500 in./year, a very high corrosion rate.

It should not be assumed that the explanation for this very large corrosion rate lies in proposing extensive mechanical cracking. On the contrary, corrosion can account for all of the metal loss necessary to produce such rapid cracking. If a crack width of 100 unit cells is assumed, a transgranular stress corrosion crack along the basal plane of the magnesium-base Jl alloy would be approximately 520Å or  $5.2 \ge 10^{-6}$  cm in width. Since, experimentally, the average rate of crack propagation during its actively cracking period was of the order of 1/8 in. in 10 min (0.03 cm/min), then in 1 min the volume of metal lost in a crack the width of the 3/16-in. specimen (0.4763 cm) would be 7.43 x 10<sup>-8</sup> cc. Using 1.8 g/cc for the density of the Jl alloy, the weight loss would be  $1.34 \ge 10^{-7}$  g.

Another approximation of weight loss can be made by using measured corrosion current values (Fig. 1). During the active portion of cracking, corrosion current flow was at least 20  $\mu$ a or  $1.2 \times 10^{-3}$ coulombs/min. By Faraday's law, the weight of metal lost should be  $1.51 \times 10^{-7}$  g.

These two weight loss approximations reduce to corrosion rates of 6,210 ipy  $(7.79 \times 10^6 \text{ mdd})$  and 7,000 ipy ( $8.77 \times 10^6 \text{ mdd}$ ), respectively, for cracks 100 unit cells in width.

Corrosion rate values thus derived strongly support the idea that electrochemical action is the primary cause and reason for the stress-corrosion cracking. These calculations, while admittedly approximate, could be considerably in error and still demonstrate the existence of extremely large corrosion rate values.

## Visual Perception of Stress Corrosion

Still another area of discussion may clarify the essentially electrochemical nature of stress corrosion cracking. Reference has been made by Harwood (5) to the motion picture produced by Priest, Fontana, and Beck (9) with respect to visual evidence of the noncontinuous nature of stress-corrosion cracking. While the motion picture does show that the crack progresses nonlinearly with time, this does not necessarily indicate a series of sharp mechanical failures triggered by corrosion. It is the writer's belief that cracking is going on continuously, but is perhaps not always continuously visible. It must be remembered that this motion picture provides only a two-dimensional view of something occurring in three dimensions. With this in mind, it is evident that noncontinuous crack propagation observed on a surface could be caused by continuous cracking taking place beneath the viewed surface. As soon as this unseen cracking progressed far enough, the surface in view would tear quickly and do so in a semiductile fashion, that is, in the manner typical of ductile metal failure at the base of a notch. This analysis is compatible with the observations recorded in the film, and it is concluded that the plastic deformation revealed in the motion picture is the result of crack 360

propagation and not the cause of crack propagation. The role of stress, then, is that of maintaining filmfree areas or, by very local deformation, causing an anodic change in electrode potential at the tip of an advancing stress corrosion crack.

## Summary and Conclusions

Much of what has been discussed refers specifically to the author's work with the Jl alloy, but the fact remains that the electrochemical nature of stress corrosion has been demonstrated for other systems as well as the work discussed in this paper. In view of experimental evidence with regard to crack corrosion rates, cathodic protection and the nature of measured corrosion currents, it seems unlikely that purely mechanical cracking plays any discrete part in the stress corrosion process unless a distinctly brittle phase exists.

It is concluded that in ductile materials transgranular stress corrosion takes place only under the driving force of a continuous electrochemical action which causes very localized removal of metal by corrosion. The site of metal removal (the crack tip) and the direction of cracking are determined by stress acting to cause localized potential differences through the interruption of film forming mechanisms or by intense, localized plastic deformation.

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# **Evaluation of the Homogeneity of Germanium** Single Crystals by Photovoltaic Scanning

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It is well known (1, 2) that photovoltages due to resistivity gradients in the bulk can exist in semiconducting crystals. This phenomenon is generally referred to as the "bulk photovoltaic effect." Resistivity inhomogeneities constitute small junctions throughout the material which allow charge separation to take place. These junctions give rise to easily observed photovoltages generally of the order of hundreds of microvolts. Photovoltages due to p-n junctions are usually in the range of tenths of a volt.

Consider, for example, an n-type germanium sample having rectangular shape with contacts at the ends. If this crystal is illuminated at some point along its length where  $(d\rho/dx) > 0$ , a voltage will be observed across the sample with the right-hand contact (at x = k) positive (left-hand contact at x = 0 grounded). Similar reasoning holds for p-type material, in which case the voltages are reversed.

Since the photovoltage depends on the existence of a resistivity gradient, it is a derivative quantity. Therefore, the integrated signal corresponds qualitatively to the changes in resistivity.

This phenomenon can be used as a sensitive and rapid tool for exploring the homogeneity of singlecrystal germanium samples that may otherwise appear to be very uniform. The experimental arrangement is shown schematically in Fig. 1. A low-speed



POTENTIOMETER

Fig. 1. Schematic of photovoltage scanning system

motor drives the crystal sample under a narrow band of white light focussed on the surface. A 40turn potentiometer is driven simultaneously, and the voltage from it drives the x-axis of the recorder. Either the direct photovoltage signal, or the integrated photovoltage as desired, is, after suitable amplification, fed into the y-axis of the recorder. A direct plot of signal versus position is thus obtained for any sample.

Figure 2 shows the experimental results for an n-type germanium sample that would ordinarily be considered as being fairly uniform over a significant part of its length. The upper curve is the photo-

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Fig. 2. Photovoltage and resistivity scan of an n-type germanium sample.

voltage scan-microvolts vs. distance along the sample in millimeters. This curve shows three points where the signal is zero, indicating that a combina-tion of three maxima and minima will occur in the resistivity curve. The lower diagram represents the resistivity scan for this sample. The solid curve is the result of integrating the photovoltage, while the circles represent the actual resistivity measurements. The resistivity measurements were taken with a two-point probe. An electrometer was used to measure voltages, and a constant-current generator supplied the sweep current to the sample. Reasonably good agreement is apparent. In the central portion of the crystal, that is, around 8 mm, the resistivity changes are of the order of 0.1%, while the photovoltages in the same region are large and distinct. It is also clear that the zero photovoltage signals coincide exactly with the maxima and minima of the resistivity curve.

To explore a crystal wafer, deep trenches are cut into the crystal on one of the large faces, in the vi-



Fig. 3. Isorho map for a p-type germanium wafer

cinity of the contacts. This procedure greatly reduces the effective lifetime of the minority carriers in the vicinity of the contact and alleviates troublesome photosignals that may arise.

Figure 3 is a diagram of such a (p-type) germanium wafer. A contact is soldered continuously along the left- and right-hand edges of the wafer. The pair of vertical lines at each end represent the trenches. A set of direct and integrated photovoltage scans (as in Fig. 2), were taken on this wafer from x = 0 to x = 22.5 mm, and y = 0 to y = 19.8 mm.

The integrated values of the photovoltage signals are plotted directly, and a resistivity map of the wafer is then prepared. The heavy lines in this map are lines connecting points of equal resistivity *change*, plotted in terms of microvolts. For convenience, let us call these lines *isorhos*. This mapping is still a very qualitative picture of the wafer. However, sufficient information can be gleaned from such a diagram so as to determine the region from which a sample having the highest uniformity can be obtained. For example, the section of the wafer in Fig. 3 between x = 0 and x = 3 mm indicates small resistivity changes as compared to other possible sections.

The section between x = 0 and x = 3 mm was cut out of this wafer and the measurements on it are shown in Fig. 4. The upper curve is the photovoltage scan, and the lower solid curve is the direct integration of it. As before, the circles represent the actual resistivity measurements. The fit between the two is clearly good.

This evaluation method has some distinct advantages over probe methods. First, it is fast; the photoscan and integration can be made in less than 1 min. Second, it is the only way known of making a detailed estimate of the homogeneity of a wafer before cutting it. Third, the photo method of estimating resistivity changes is applicable under conditions where probe methods are very difficult, as, for example, when the sample is held at liquid nitrogen temperatures.

Thus far there has been reasonable success in obtaining relative values of resistivity changes by photoscanning. By taking into account such important factors as the lifetime of the material, the photo-



Fig. 4. Photovoltage and resistivity scan of a filament cut from the wafer of Fig. 3.

voltaic scanning method should be suitable for approximating the actual values of the resistivity changes in ohm-centimeters.

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# **Production of Electrolytic Copper Powder**

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ABSTRACT

A detailed description of the operation, equipment, and quality control used in the commercial production of electrolytic copper powder<sup>2</sup> is presented. The effect of electrochemical and mechanical variables on the physical characteristics of electrolytic copper powder is also reviewed.

Roll has discussed (1) the advantages and improved properties obtainable by the use of electrolytic metal powders. The present paper describes the production of electrolytic copper powder. The plant<sup>3</sup> is an integrated copper smelter and refinery which processes concentrates, blister and scrap to fire refined, electrolytic and OFHC<sup>4</sup> brand copper. In addition to electrolytic copper powder, the plant also produces atomized copper-lead based powders as well as solder and tin powders.

Electrolytic copper powder, based on the work of Drouilly (2), has been produced by the refinery for twenty-five years. During this period the production capacity of copper powder was increased from 20,000 to over 1,000,000 lb/month. Simultaneously, with increased production capacity, many improvements have been made in production and control techniques, resulting in a better and more uniform product.

The physical characteristics such as particle size, apparent density, flow rate, and dimensional change on sintering of electrolytically deposited copper powder are affected by a number of factors. The most important of these are the current density, copper and acid content and the temperature and circulation rate of the copper sulfate electrolyte. Although electrochemical variables can be controlled to produce a powder within a relatively narrow range of physical properties, they cannot be controlled sufficiently to yield a product which meets the rigid specifications required by the consumer. Consequently, further processing operations on the washed powder are required such as furnacing in a controlled atmosphere, grinding, screening, and blending.

The basic electrochemical theory of electrorefining and electroplating is identical to that of electrolytic powder deposition. The electrochemical conditions affecting the type of deposit, however, are controlled in powder production so as to yield a deposit which is the opposite of that desired in refining and electroplating where a hard, dense and smooth, adherent cathode is the object. An excellent paper on the theories covering metal powder deposition has been presented by Mehl (3). Wranglen (4) also defines the three basic factors responsible for the formation of powdery and spongy deposits as low metal overvoltage, depletion of the metal content of the cathode film, and the formation of basic material in the cathode film. Only the first two factors are of importance in this case.

While the generalities noted above do produce spongy deposits, it is necessary to control the following variables to produce a powder within a specified range of physical properties. These are: (a) electrolyte composition (acid and copper content); (b) electrolyte temperature; (c) electrolyte circulation rate; (d) current density; (e) size and type of anode and cathode; (f) electrode spacing; and (g) brush-down interval.

The last variable is very important since it not only controls the type of deposit which builds up on the cathode, but also prevents excessive variations

Table I. Effect of brush-down interval

Brush-down interval, hr	Apparent density, g/cc	Dimensional change, %
1	2.15	0.55
4	2.18	0.58
8	2.35	1.62

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<sup>\*</sup> Registered trademark of American Metal Climax, Inc.

Table II. Effect of temperature Cu in bath, 8.5 g/l

Temperature, °C	Apparent density, g/cc	Dimensional change, %
50	2.15	0.55
55	2.40	1.75
60	2.70	2.12
65	2.85	2.50

Table III. Effect of copper content in bath; temp, 55°C

Copper content, g/l	Apparent density, g/cc	Dimensional change, %
5	1.90	1.13
6	2.05	1.30
7	2.18	1.44
8	2.32	1.60

in the cathode area, with consequent lowering of the current density. Tables I, II, and III indicate the effect of three of the above variables on the apparent density and the per cent dimensional change on sintering.

## **Electrolytic Operations**

A section of the regular electrolytic copper refining plant, or tank house, is used for the production of electrolytic copper powder. The powder section uses the same type of cell as is found in the regular tank house and is also supplied with direct current from the main power plant. Electrolyte and electrical conditions for the two units are different, but by suitable alteration of piping and bus bars, sections can be switched from electrolytic copper refining to powder production and vice versa. This flexibility allows for considerable leeway in operating capacity of the two units.

At the present time, six sections or groups of cells, containing 16 cells each, are available for powder production. In addition, copper powder is also produced by four-cell liberator sections which control the electrolyte copper content by plating from the electrolyte solution instead of from copper anodes. The cells of four of the regular sections are constructed of wood, with adjacent cells having common side walls. The dimensions are 11 ft long by 31/2 ft wide by 4 ft high (I.D.). These tanks are completely lined with 8-lb, 6% antimonial lead. The remaining two regular sections and the liberators are made of individual self-supporting, glass-fiber reinforced, polyester cells. The plastic cells are superior to the lead-lined cells from an electrical viewpoint, since stray currents and current leakage are minimized. To evaluate plastic tanks for use in the powder plant several different design and fabrication methods were used. While several units have demonstrated excellent serviceability, other tanks have developed leaks due to separation of the fiber-glass laminations. Repairs to these tanks is an arduous task since it is difficult to determine where the leak originates in the laminated structure.

All cells are supported by concrete piers standing in the basement floor. For electrical insulation from the ground, the columns are capped with glass and are protected from electrolyte leaks by plastic shields. Each cell is equipped with a solution outlet 15 in. from the bottom for partial draining. This outlet, in conjunction with a stand pipe which controls the solution level in the tank, is also used as an outlet for the circulating electrolyte. Another outlet in the cell bottom is used for complete draining.

Originally the sections were built on two levels so that the electrolyte flowed from the tank in the upper tier to the lower lying parallel tank before returning to storage for recirculation. Due to the change in both copper content and temperature of the electrolyte in flowing through the two tanks, powder deposited in the lower section was much coarser and heavier. To overcome this nonuniformity in powder production, all sections are now built on the same level and each tank has individual circulation. Electrolyte is pumped from basement storage tanks to an elevated head tank. From there it flows to manifolds on each section by gravity, and then into the back and the top of the cell. Thus circulation of electrolyte in the tanks is top to bottom. This yields a finer, more homogeneous powder than bottom to top circulation. Electrolyte returns to the basement storage by gravity.

The cathodes, which have been the subject of considerable experimentation, are now 6% antimonial lead,  $24 \times 34 \times 36$  in. and weigh about 150 lb each. Polished copper, aluminum, stainless steel, rolled and cast lead, as well as carbon, have been tried but none proved as satisfactory as the presently used material. For better contact, these cathodes are cast directly on the  $\frac{1}{2} \times 1\frac{1}{2} \times 46$  in. copper bars by which they are suspended. The lead cathodes have an average life of several years.

Each cell is loaded with eighteen lead cathodes at a spacing of 7 in. centers, and nineteen copper anodes which are hung between the cathodes. The electrodes in each cell are in parallel with each other, and the cells and sections are in series with each other. The bus bars from which the electrodes hang are notched, which prevents the electrodes from shifting and also gives better contact, permitting 20% higher amperage operation.

Power is supplied to the cells by a 1500 kw motor generator set at 10,000-13,000 amp, the power being conducted to the cells by a 21 square inch bus bar. At 12,000 amp, the current density on the anodes is 50 amp/ft<sup>2</sup>.

During electrolysis, some of the deposited powder sloughs off and falls to the bottom of the cell. To prevent short circuiting between anodes and cathodes, causing a decrease in cathode current density and deposition of large particles, the cathodes are brushed down periodically with a long handled rubber squeegee. Several other methods such as continuous vibrating, shaking, and hammering have been tried, but none has been practicable.

At the end of the three-day operating cycle the power is turned off in that particular section. The electrolyte is drained to a level just above the top of the powder. The anodes and cathodes are washed down and removed from the cells by an overhead crane which services the entire powder section. The bottom outlet is opened and the remaining electrolyte drained from the tank along with a small amount of powder which is later cleaned from the solution launders.

The powder is scooped from the bottom of the cell by a motorized clam-shell bucket attached to the overhead crane. Damage to the cell bottom is prevented by wooden or plastic boards placed in the cell.

The subsequent powder washing operation is one of the most important steps in the whole production cycle. All traces of electrolyte must be removed from the powder, otherwise an impure and easily oxidizable material will be produced. In addition, any sulfate remaining in the powder will cause repeated breakdowns in the electrically heated furnaces used in the finishing operation. Until several years ago, a 40-in, batch type Tolhurst centrifuge was used to remove the electrolyte from the wet powder, followed by a clean water wash. Due to the high speed of the centrifuge, the powder was compacted causing particles to densify, making production of low density powder impossible. Production of low density powder was possible only by percolation washing in wooden boxes. Due to channeling, washing was frequently poor, and consequently time-consuming to achieve complete removal of electrolyte.

A system of washing and dewatering has been developed which improves the copper powder operation immensely. The present system, which is operating very efficiently, involves dumping of the powder from the clam-shell bucket into a 400 cubic foot tank. Water is added to slurry the powder which is then pumped by a Wilfley centrifugal pump to one of two 400 cubic foot surge tanks. Here, the slurry is adjusted to the proper consistency and then pumped to a 60 in. diameter horizontal Oliver continuous filter. The filter dewaters the slurry, washes it twice with clean water, and then dewaters it to about 20% moisture. A rotating screw removes the moist powder from the filter.

Since the density ratio of powder to solution is approximately 8:1, special precautions must be taken to prevent settling of powder in pipes, tanks, pumps, valves, etc. Although considerable preliminary test work was done to determine critical velocities and powder characteristics after pumping, a lengthy start-up period was needed in the plant before trouble-free operation was obtained. The irregular structure of the powder complicated matters even more, since once powder starts to settle out in the system, the powder particles interlock resulting in a very solid and hard-to-remove plug.

All equipment external to the cells is constructed of stainless steel type 316 and has given satisfactory service.

Because of the low acid content and relatively low temperature of the electrolyte, as well as the high resistance of the lead cathodes and high current density used, the power consumption is considerably higher than for copper refining. The average voltage per tank is 0.9-1.1 v compared to normally less than 0.25 v for copper refining. The ampere efficiency at the anode is in excess of 95%, but at the cathode it is somewhat less than 90% because of the deposition of hydrogen and relatively rapid redissolution of fine copper powder.

## Preparation

The wet powder, which oxidizes readily because of its finely divided state and active surface, is now ready for the finishing operations. Certain of its properties, especially the apparent density and the dimensional change on sintering, have been produced in the powder during electrodeposition. To produce an acceptable grade of powder, however, a furnacing operation followed by grinding and screening with subsequent blending of the finished powder is needed.

As in the electrolytic operations, considerable improvements have been made in the processing division. When operations were begun in 1932, 6-in. tube furnaces were used to treat the powder. Small boats held the wet powder and were pushed through the furnace by hand. As demand increased and better equipment became available, the first of a series of four chain-driven pan furnaces was installed in 1937. These furnaces are 60 ft over-all in length having a three-section, 30-ft electrically heated zone and a 30-ft water jacketed cooling zone. Manually filled and compacted paper-lined copper pans were used to hold the powder. In order to meet increasing demand and to achieve improved production methods, a mesh belt furnace was installed in 1951 to supercede the pan-type furnaces. Various other improvements were also made in the grinding and classifying system.

Due to the location of the electrolytic production unit and the processing plant, the filtered product must presently be transported to the finishing division. A ten-ton fork lift truck which carries three boxes per trip is used for this job. Pumping has been considered, but, because of the difficulties encountered in even the short distance pumping in the tank house, improved systems must be developed before this will be feasible. Added factors are the possible and very probable detrimental changes that long distance pumping will have on powder characteristics.

Powder is dumped from the transfer boxes into the charge hopper of the mesh belt furnace. Dimensions for this furnace are identical to the above described pan furnaces. The continuous mesh belt, made of Cambriloy 25-20 alloy wire, is driven by a variable speed drive and operates at 1-7 in./min. To prevent wet powder from falling through the belt, a continuous high wet strength paper sheet is interposed between the belt and the powder. A roller after the charge hopper compresses the powder to improve heat transfer and to prevent loose powder from falling off the belt. After the belt enters the furnace and all water has been driven off, the paper burns, but by this time the powder has sintered sufficiently to prevent any of it from falling through the meshes of the belt.

Furnace atmosphere is produced in exothermic gas producing units.<sup>5</sup> Natural gas and air are burned in a ratio of approximately 1:6 to give a gas con-

<sup>&</sup>lt;sup>5</sup> General Electric Co.

taining 17% H<sub>2</sub>, 12% CO, 4% CO<sub>2</sub>, balance N<sub>2</sub>. Refrigeration lowers the dewpoint to 30°-40°F. Gas is fed to the furnace counter-currently, which improves reduction and improves cooling of the cake.

The furnace operation accomplishes the following: (a) drying the powder; (b) reducing oxide; (c) sintering the fines; (d) altering physical properties including apparent density and sintering characteristics.

By varying furnacing temperature between  $900^{\circ}$ -1450°F and concurrently varying furnacing time by changing the belt speed, large changes in the amount of fines, the apparent density, and to some extent the dimensional change characteristics can be effected. This furnacing operation is consequently the second point where powder properties can be changed to meet final specifications.

Depending on furnace conditions, the sintered powder discharges as a soft to a hard cake which cannot be broken by hand. Discharge temperature is maintained low enough to prevent re-oxidation of the powder. As the cake discharges, it is broken by grappling hooks and given a preliminary crushing in a 40 hp hammer mill to  $\frac{1}{4}$  in. The crushed cake is next lifted to the main grinding system by a bucket elevator.

Fine grinding is done by Mikro-Pulverizers. These are high-speed water-cooled hammer mills equipped with Stellite faced hammers. Feed rate to the mills, the mill speed, and the screen opening under the mill can all be varied to obtain the desired powder characteristics. Normal operating conditions are: (a)3000 - 4500 rpm; (b) 500 - 1000 lb/hr mill; (c)1/16 - 3/32-in. screen opening; (d) screen hole shape: round, elliptical, slots.

The grinding operation becomes the third operation where powder characteristics can be changed. Each grinding system consists of two Mikro-Pulverizers in series. One or both units can be used to grind the powder, depending on the type desired. The ground powder is then moved to screen hoppers. These discharge into Sprout Waldron bolting reel screens equipped with a beater arm. Oversize powder from the screen is returned to a secondary grinding system which again consists of two Mikro-Pulverizers and screen. The minus 100 mesh powder is next classified in a Gayco air classifier. Fines from this unit are collected in 24-gal drums and moved to the blending floor. Oversize from the air classifier can either be removed from the system or, if desired, be again returned to the grinding system.

The grinding and classifying system consists of seven banks of Mikro-Pulverizers, screens, air clas-

sifiers, and the necessary bucket elevators and screw conveyors. Ground material starts in the first unit, and oversize, or material for regrinding to change its characteristics, is then ground and classified progressively through the whole system. The product from the final unit has been worked considerably and represents the highest density material produced. Its apparent density is above 3.5 g/cc and its application is for specialized uses. Oversize from this system is rejected and sent to the casting building for remelting.

Powder that discharges from the system is stored in closed drums to which silica gel containers are added to control humidity and prevent oxidation. Each drum of powder is sampled and its weight, apparent density, flow, and screen characteristics recorded.

To produce a lot of finished powder to meet customer specifications, the correct type of powder is selected from the storage drums and mixed in one of three Gemco double cone blenders. The lot size is generally 20,000 lb/blender charge and, before a lot is withdrawn from the blender into shipping drums, all specifications have been checked by the Control Department and approved for shipment.

In order to control all phases of the operation, a well-equipped production control laboratory is maintained. The control laboratory checks both electrolytic and finishing operations and the following samples are taken and tested.

1. Daily composite of cell powder: Tested for particle size distribution, flow, and apparent density.

2. Electrolyte sample: Tested for copper content and acidity.

3. Daily composite of filtered powder: Tested for washing, particle size, flow, apparent density, dimensional change on sintering, and sintered strength.

4. Hourly furnace discharge cake: Tested for temperature.

5. Shift composite of discharge: Analyzed for oxygen content.

6. Daily composite of furnace production: Tested for particle size distribution, apparent density, oxygen content, dimensional change on sintering, and sintered strength.

7. Daily composite of finished production lots: Tested for chemical assay: Cu, Pb, O<sub>2</sub>, C, S, HNO<sub>3</sub> insol., grease.

8. Daily composite of main finished powder production: Tested for screen analysis, flow, apparent density, and dimensional change on sintering.

**Table IV. Powder specifications** 

Л Туре	Apparent		Screen analysis			Chemical analysis %		
	g/cc	sec/50g	+100 mesh	-325 mesh	change, %	Cu	H <sub>2</sub> loss	HNO <sub>3</sub> insol.
LC	1.5-1.75	(Scott)	0.1 Max.	90 Min.	_	99.0 Min.	0.75 Max.	0.03 Max.
C	2.1-2.5	(Scott)	0.1 Max.	90-95 Min.		99.0 Min.	0.75 Max.	0.03 Max.
A	2.4-2.6	32 Max.	0.5 Max.	22-32		99.5 Min.	0.30 Max.	0.03 Max.
в	2.5-2.6	32 Max.	0.2 Max.	43-53		99.5 Min.	0.30 Max.	0.03 Max.
U	2.5-2.6	35 Max.	0.2 Max.	55-65	0.3-1.8	98.4	0.40 Max.	0.03 Max.
HM	2.6-2.7	35 Max.	0.2 Max.	60-70		99.25	0.50 Max.	0.03 Max.
AJL	3.5-4.0	24 Max.	0.8 Max.	35-45		99.25	0.30	0.03 Max.

9. Monthly composite of finished production lots: Tested for tensile strength and green strength.

10. Production lots: Tested for screen analysis, apparent density, flow, dimensional change on sintering, green strength, and chemical assay.

This amount of testing has been found necessary to give a satisfactory degree of control over all operations and to assure consistent uniform powder production.

Table IV shows some of the types of powder produced. These range from the very light and fine LC type to the heavy and coarse material which is designated AJL. All other grades produced lie between these types.

To supplement the control section, a fully equipped powder research laboratory is also maintained. This unit has the responsibility of developing and improving production methods and to assist the operations generally. Since the United States Metals Refining Company also produces other powders, the laboratory has units for producing atomized powders. and an electrolytic section which consists of electroplating tanks which range in size from battery jars to full size units. The laboratory is also fully equipped with presses and sintering furnaces to study the effect of all processing variables on finished product characteristics. Process variables can consequently be fully evaluated in the laboratory before large scale tests are made in the production unit.

Manuscript received Oct. 13, 1958. This paper was repared for delivery before the Buffalo Meeting, Oct. 6-10, 1957.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1959 JOURNAL.

#### REFERENCES

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## Alvin J. Salkind and William C. Zeek

The Electric Storage Battery Company, Research Center, Yardley, Pennsylvania

The structure of silver oxide (AgO) has been of interest to members of the Society as evidenced by recent articles (1) in the Journal, and by discussions at the Ottawa Meeting.

We would like to draw the attention of readers of this Journal to a group of researchers whose earlier contributions to this field are often overlooked. We refer to the work of Vladimiro Scatturin and his associates at the University of Padua. Their most recent paper was entitled "The Crystalline Structure of AgO" (2).

They investigated the crystal structure of AgO using both copper and iron radiation and listed in their paper 36 reflections obtained with Fe K $\alpha$  radiation. They were able to index all these reflections by the Ito method and concluded that the compound was monoclinic, Space Group  $C_2^{*} h = C 2/C$  with the following parameters.

a =	5.85 <sub>2</sub> Å	b =	3.478	$c = 5.49_{5}$
β =	107°30'	$\mathbf{V} =$	106.7Å <sup>3</sup>	$\mathbf{Z} = 4$

The authors also discussed the position of the atoms and concluded that with the atoms as follows:

 $4 \text{ Ag in } \frac{1}{4}, \frac{1}{4}, 0; \frac{3}{4}, \frac{1}{4}, \frac{1}{2}; + (000; \frac{1}{2}, \frac{1}{2}, 0)$ 

 $4 \text{ O in } 0, Y, \frac{1}{4}; 0, Y, \frac{3}{4}; + (000; \frac{1}{2}, \frac{1}{2}, 0)$ 

the most probable value for the parameter Y was 0 084

Comparisons are also drawn with the spacings commonly found in other silver compounds.

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- 2. V. Scatturin, P. Bellon, and R. Zannetti, "La Ricerca Scientifica 7" 2163 (1957).

## Oxidation of Aqueous Ferrous Sulfate by Glow Discharge

H. A. Dewhurst, J. F. Flagg, and P. K. Watson

Research Laboratory, General Electric Company, Schenectady, New York

A variety of chemical reactions may be produced in aqueous solution by "glow discharge electrolysis." The observed chemical effects have been attributed to ions which are produced in the vapor phase by the discharge (1-3). It is well known that in glow discharges several chemically active species are formed in addition to the ions. These include atoms, radicals, metastables, as well as photons, all of which can, under favorable conditions, produce chemical reactions in aqueous solution. We have recently carried out experiments which were designed to differentiate between the effectiveness of the positive ions and of the electrically neutral species in the glow discharge oxidation of ferrous sulfate. The portion of the total oxidation attributable to charged species was determined by interposing a platinum grid between the discharge point and the solution. The grid was used as the negative electrode in the cell so that it collected the positive ions from the discharge. However, because of its open construction, it had very little effect on the electrically neutral species.

The discharge cell was similar to that used by Hickling and Linacre (2) with the exception of the grid and the fact that the platinum cathode was placed directly in the aqueous solution. The anode was a stainless steel hypodermic needle situated approximately 1.0 cm above the surface of the solution. Deaerated 0.01M ferrous ammonium sulfate solutions (5-10 ml) 1.0N in H<sub>2</sub>SO<sub>4</sub> were used. The amount of oxidation was determined by spectrophotometric measurement of ferric ion at 305 mµ (4). The total current was measured with a Keithley electrometer. Oxidation yields are reported in terms of the number of equivalents of ferric ion produced per Faraday of charge. Experiments were carried out at about 25 mm pressure under which conditions the discharge operated in water vapor. Other ex-

Table I. Glow discharge oxidation of aqueous ferrous sulfate  $Fe^{z_{\star}}=0.01M$  in 1.0N  $H_{a}SO_{4}$ 

Voltage, kv	Current, µamp	Fe <sup>3+</sup> Ior Grid*	ns/Faraday No Grid
1.1	100	0.6	25
1.2	1000	0.3	11
0.65	4200	0.2	11
10.5	50	5.5	13.5
4.2	8.5	0.8	8.7†
4.8	50	1.4	9
7.0	100	0.9	10
	Voltage, kv 1.1 1.2 0.65 10.5 4.2 4.8 7.0	Voltage, kv         Current, µamp           1.1         100           1.2         1000           0.65         4200           10.5         50           4.2         8.5           4.8         50           7.0         100	Voltage, kv         Current, amp         Fe <sup>8+</sup> Ior Grid*           1.1         100         0.6           1.2         1000         0.3           0.65         4200         0.2           10.5         50         5.5           4.2         8.5         0.8           4.8         50         1.4           7.0         100         0.9

3 mil wire, 80 wires/in.
 † Current was 4.0 μamp.

periments were conducted at 760 mm pressure with either a static or flowing (3 liters/min) atmosphere of pure nitrogen. The results of these experiments are shown in Table I.

Results at low pressure show that species removed by the grid account for at least 95% of the observed oxidation. The inverse dependence of the oxidation yield on current will be discussed in a later publication. We note that yields under our conditions are greater than yields observed by Hickling and Linacre (2).

Results at 760 mm pressure under static conditions show that about 60% of the oxidation could be accounted for by species removed by the grid. Under flow conditions, however, the grid prevented about 90% of the oxidations. We attribute the decreased effectiveness of the grid under static conditions to the presence of water vapor in the discharge region. In other experiments it was observed that under flow conditions presaturation of the nitrogen with water increased the yield to that obtained under static conditions.

In connection with these studies we have also examined the effect of various gases, ferrous sulfate concentration, and polarity on the yields. An oscillographic study has been made of the electrical characteristics of the discharge, under conditions used in these experiments. Details of these and related studies will appear in a subsequent publication.

### Acknowledgment

The authors wish to acknowledge helpful discussions with Dr. K. H. Kingdon.

Manuscript received Nov. 17, 1958.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1959 JOURNAL.

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## Correction

In the December 1958 issue of the JOURNAL, page 728, paper entitled "Electron Mobility in InP," the

authors' names should be M. Glicksman and K. Weiser. Dr. Glicksman's name was misspelled.

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# FUTURE MEETINGS OF The Electrochemical Society

g

Philadelphia, Pa., May 3, 4, 5, 6, and 7, 1959

Headquarters at the Sheraton Hotel

Sessions will be scheduled on Electric Insulation, Electronics (Including

Luminescence, Semiconductors, Thermionics, and Devices), Electrothermics and Metallurgy,

Industrial Electrolytics, and Theoretical Electrochemistry

\* \* \*

## Columbus, Ohio, October 18, 19, 20, 21, and 22, 1959

Headquarters at the Deshler-Hilton Hotel

Sessions probably will be scheduled on

Batteries, Corrosion (including a joint Corrosion-Electronics-Semiconductors session),

Electrodeposition (including symposia on "Electrodeposition from Organic Solvents"

and "Electro- and Chemical-Polishing"),

Electronics (Semiconductors), Electro-Organics,

and Electrothermics and Metallurgy

\* \* \*

Chicago, Ill., May 1, 2, 3, 4, and 5, 1960

Headquarters at the Lasalle Hotel

\* \* \*

Houston, Texas, October 9, 10, 11, 12, and 13, 1960

Headquarters at the Shamrock Hotel

\* \* \*

Papers are now being solicited for the meeting to be held in Columbus, Ohio, October 18-22, 1959. Triplicate copies of each abstract (not exceeding 75 words in length) are due at Society Headquarters, 1860 Broadway, New York 23, N. Y., not later than June 1, 1959 in order to be included in the program. Please indicate on abstract for which Division's symposium the paper is to be scheduled, and underline the name of the author who will present the paper. Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at 1860 Broadway, New York 23, N. Y. Current Affairs



# Gardiner, LaQue, and Campbell to Take Office in Philadelphia



W. C. Gardiner

As a result of the recent annual election, in which the voting is by mail ballot, William C. Gardiner has been elected the new President of The Electrochemical Society; Frank L. LaQue, third Vice-President; and Ivor E. Campbell has been elected Secretary. They will take office at 8:00 A.M. on Thursday, May 7, 1959, in Philadelphia at the Spring Annual Meeting of the Society.

Dr. Gardiner, manager research engineering, Research and Development Dept., Industrial Chemicals



F. L. LaQue

Div., Olin Mathieson Chemical Corp., Niagara Falls, N. Y., replaces Sherlock Swann, Jr., research professor of chemical engineering at the University of Illinois, Urbana, Ill. Dr. Swann, as Past President, will continue as a member of the Board of Directors.

Frank L. LaQue, a vice-president, and manager of the Development and Research Div., International Nickel Co., Inc., New York City, will start the first year of his three-year term as Society Vice-President, and



I. E. Campbell

will serve with the two previously elected Vice-Presidents, Ralph A. Schaefer and Henry B. Linford.

Ivor E. Campbell, formerly of Battelle Memorial Institute and now director of research and development, National Steel Corp., Weirton, W. Va. (see following item), will begin the first year of his three-year term as Secretary of the Society. He has been serving as Interim Secretary, by Board appointment, since January 1959, succeeding Henry B. Linford who had held the post since 1949.

# I. E. Campbell Appointed Director of Research and Development at National Steel Corp.

Ivor E. Campbell recently assumed the position of director of research and development at the National Steel Corp., Weirton, W. Va., succeeding J. H. Strassburger who has been advanced to vice-president, research and development. Dr. Campbell formerly was with the Battelle Memorial Institute in Columbus, Ohio.

Earlier this year, Mr. Strassburger instituted an expanded and coordinated program of research and development which is being conducted both on a corporation-wide basis and in the various subsidiary companies of National Steel. The program involves continuous study and development work on raw materials, facilities, processes, and finished products. Dr. Campbell will directly assist Mr. Strassburger in the administration of all phases of the program. The research and development department is now occupying temporary quarters in a separate building in Weirton, pending construction of a permanent National Steel research center. The country's fifth largest steel company, National Steel is a major producer of hot and cold rolled sheets, tin plate, zinc coated steel, and other steel products. It also produces merchant pig iron and manufactures and distributes nationally a line of steel buildings, nailable steel flooring for railroad cars, and organic and vinyl coated steels.

Since 1950, Dr. Campbell had been chief of the Div. of Inorganic Chemistry and Chemical Engineering of Battelle Memorial Institute. He

joined the Battelle staff in 1943 as a research chemist and advanced to assistant supervisor of the Div. of Nonferrous Metallurgy in 1948.

His major interests have been in the development of improved processes for the preparation of highpurity metals and in the formation of refractory coatings by vapor-deposition techniques. He also has worked extensively with iodide-refining processes for metals.

He is the author of more than 30 articles in scientific and trade journals, dealing principally with vapor plating and with the preparation and properties of high-purity metals and refractories. He is coauthor of The Electrochemical Society's monograph "Vapor Plating" published in 1955, and editor of "High Temperature Technology" published by John Wiley, as part of the Society's monograph series, in 1956.

Dr. Campbell, who is the newly elected Secretary of The Electrochemical Society for a three-year term, will formally take office at the Philadelphia Meeting in May. By Board appointment, he has been Interim Secretary since January.

## Plans for Philadelphia Meeting Completed



E. G. Enck



G. W. Bodamer

man. The sub-committees are as follows: Hotel Arrangements, Edgar L. Eckfeldt, Chairman: Registration, E. Charles Evers, Chairman; Finance, G. Franklin Temple, Chairman; Entertainment, John G. Miller, Chairman; Publicity, Harry C. Mandell, Jr., Chairman; Ladies' Program, Mrs. Ernest G. Enck, Chairman.

#### Entertainment

Philadelphia is a fascinating combination of the old and the new. Within a mile or two of Convention Headquarters, the history of this country was made. Maps and booklets showing what to see and how to get there will be provided at the registration desk.

The formal entertainment pro-



E. L. Eckfeldt



E. C. Evers

gram will begin on Monday evening with a Get-Acquainted Mixer in the Hotel Ballroom.

The Tuesday Luncheon of the Society will be addressed by Dr. Roy F. Nichols, vice-provost and dean of the Graduate School of Arts and Sciences, University of Pennsylvania. Dr. Nichols is a noted historian, a Pulitzer Prize winner, and an outstanding speaker.

On Tuesday evening, the Annual Banquet will feature a talk on the Society by President Sherlock Swann, Jr; the introduction of new Honorary Members by Past President J. C. Warner; and special recognition of "Old Timers," the veteran mem-bers who have, through the years, helped to advance the Society to its



SS State of Pennsylvania, chartered by the Society for a trip on the Delaware River on Wednesday, May 6.



The completed program for the 115th Meeting of The Electrochemical Society, to be held at the Sheraton Hotel, Philadelphia, May 3 to 7, 1959, indicates that this will be one of the best all-round conventions of the Society in its 57 years of progress.

The Sheraton, Philadelphia's newest hotel, was designed to accommodate large conventions and provides excellent facilities for technical sessions, committee and section meetings, and for all the details that go to make a successful meeting.

Registration will commence on Sunday, May 3, from 3:00 to 9:00 P.M. Registration headquarters will be open from 8:00 A.M. to 4:00 P.M. on May 4, 5, and 6, and from 8:00 A.M. to Noon on May 7.

Technical meetings are scheduled from 9:00 A.M. to 5:00 P.M. from Monday, May 4, to Thursday, May 7, inclusive. Sessions will be held simultaneously on Electric Insulation, Electronics, Electrothermics and Metallurgy, Industrial Electrolytics, and Theoretical Electrochemistry. The detailed program was published in the March JOURNAL, pp. 45C-76C.

The Philadelphia Section, which is host to this meeting, has had its Convention Committee working on arrangements for more than a year. This committee is headed by Ernest G. Enck, General Chairman, assisted by George W. Bodamer, Vice-Chair98C

## JOURNAL OF THE ELECTROCHEMICAL SOCIETY

April 1959



G. F. Temple



J. G. Miller



H. C. Mandell, Jr.



Mrs. E. G. Enck

present high position in the scientific world.

On Wednesday evening, at 6:00 P.M., the Society will turn nautical and take over the 225-foot steamer. "State of Pennsylvania." of the Riverview Lines for an evening's trip down the active and picturesque Delaware River. Guides will point out the numerous interesting sights, such as the Naval Shipyard, where many of the nation's greatest warships have been built; Fort Mifflin (where in 1777 an American garrison held at bay an army of 12,000 British); the New York Shipbuilding Corporation, on the Camden side, where the NS Savannah, the world's first atomic surface vessel, is under construction.

A buffet supper will be served, followed by dancing to the music of one of the top bands, together with the awarding of prizes and other features arranged by the Committee.

While the Committee is doing everything possible to insure good weather on the evening of May 6, the trip will be made, rain or shine. Three of the four decks of the "State of Pennsylvania" are enclosed, and outside weather will not put a damper on the progarm arranged.

#### Ladies' Program

For the entertainment and edification of the ladies attending the convention, the committee headed by Mrs. Ernest G. Enck has prepared an excellent program for Monday, Tuesday, and Wednesday. On each of these days, there will be a get-together coffee hour in the morning. On Monday afternoon there will be a guided bus tour of historic Philadelphia, or a visit to the Robert Tait McKenzie exhibit at the University of Pennsylvania, Tuesday's schedule includes luncheon at the Dupont Country Club in Wilmington, Del., followed by a trip to "Winterthur," the nationally famous estate of Henry Francis duPont. On Wednesday, lunch at the Philadelphia Cricket Club, a visit to the stainedglass studio of Henry Lee Willets, and a stop at the Morris Arboretum are scheduled.

## International Symposium on Electrode Processes

A three-day Symposium on Electrode Processes to be held in Philadelphia on May 4-6, 1959 has been organized by the Theoretical Electrochemistry Division of The Electrochemical Society as part of the program of the Spring Meeting of the Society. Substantial support was obtained from the Air Force Office of Scientific Research, Air Research and Development Command.

A distinguished group of speakers will present papers: Barker (Harwell), Bockris (Philadelphia), Breiter (Munich), Conway (Ottawa), Frumkin (Moscow), Gierst (Brussels), Horiuti (Sapporo, Japan), Kolotyrkin (Moscow), Levich (Moscow), Llopis (Madrid), Marcus (Brooklyn), Parsons (Bristol), Piontelli (Milan), Randles (Birmingham, England), Vetter (Berlin), and Yeager (Cleveland). A paper prepared by D. C. Grahame (Deceased), A. E. Higinbotham, and F. R. M. Deane (Amherst) will be presented by Dr. Parsons.

The program was planned to allow ample time for discussion. Only a few American and Canadian speakers are included to avoid crowding of the program. Polarography and anodic films were not included for the same reason. These aspects of electrode processes have been or will be covered at other international meetings (Heiligenberg, Cambridge, etc.).

Presentation of papers will be limited to one-half the time allotted to each speaker, the other half being reserved for discussion and short presentation of related material by the audience. It is hoped that this emphasis on audience participation will result in a stimulating and interesting meeting. Papers and discussions will be published as a monograph to be edited by Professor E. Yeager, Dept. of Chemistry, Western Reserve University, Cleveland, Ohio. Discussion material (communicated) can be sent to Professor Yeager before May 15, 1959. Publication delay will be reduced to a minimum.

Topics to be discussed include double layer phenomena, correlation between double layer structure and electrode kinetics, electrode reaction mechanisms, hydrogen overvoltage, rapid reactions, single crystal studies, isotopic effects, metal deposition and dissolution, convective diffusion, etc. For the complete list of titles and program see the March JOURNAL, pp. 45C-76C.

A booklet of 1000-word extended abstracts (with bibliography) is available at \$3.00 from Dr. Ralph Roberts, 3308 Camalier Drive, Washington 15, D. C.

Extended abstracts of papers for the general session, May 7, are included.

P. Delahay, Symposium Chairman

## International Symposium on Liquid Dielectrics

An International Symposium on Liquid Dielectrics has been scheduled as part of the program of the Electric Insulation Division of The Electrochemical Society at the 115th National Meeting of the Society in Philadelphia, May 3-7, 1959.

The object of this Symposium is to provide a meeting place to consider current ideas regarding the mechanisms of the electrical breakdown of liquid dielectrics and of the conduction and loss phenomena in such media. The understanding of the basic processes involved in breakdown, conduction, and loss phenomena is of considerable interest to many aspects of the technology of the electrical industry.

A number of topics will be discussed both from an experimental and a theoretical viewpoint. In regard to breakdown phenomena, these include studies of the dependence of breakdown on the type of applied stress; the relationship of molecular structure to breakdown strength; the importance of electrode material, electrode surface condition, gas adsorption at the electrode in the breakdown process, as well as the influence of pressure; and the gassing tendency of dielectrics.

Investigations of the conduction and loss phenomena consider the influence of water and gas in the insulating liquid: conduction under pulse conditions; electron mobility in liquids; electron emission from the electrode. The systems to be considered include simple, single hydrocarbons: complex natural materials such as the mineral oils; and synthetic fluids such as the silicones and chlorinated aromatics. The contributions, though stressing the fundamental aspects of the phenomena, are also concerned with conditions found in practice.

It may be noted that the most recent comprehensive study, published in English pertinent to the subject matter of the proposed Symposium, is now over 25 years old. This is a monograph by A. Gemant entitled "Liquid Dielectrics." It is intended that the papers presented at the Symposium will be published as an independent monograph or volume of collected papers and serve to bring the subject matter of the field up to date.

The speakers from abroad include representatives from both academic and industrial laboratories. The timeliness of such an international meeting is emphasized by the fact that such a meeting has not been held for a long time. The last meeting, on a more limited scale and including liquid dielectrics as a small part, was a symposium of the I.E.E. in London in 1953. The enthusiastic support by the co-sponsors, the National Science Foundation and the Office of Naval Research, has insured the participation of academic speakers American scientists and engineers will look forward to the exchange of ideas with their foreign counterparts.

The planners of this Symposium include: Louis J. Frisco, Chairman of the Electric Insulation Division of The Electrochemical Society, Johns Hopkins University, 1315 St. Paul St., Baltimore 2, Md.; Thomas D. Callinan, Secretary-Treasurer of the Electric Insulation Division, International Business Machines Corp., Yorktown Heights, N. Y.; and Harold Basseches, Chairman of the Symposium, Bell Telephone Labs., Inc., Murray Hill, N. J. Further information may be obtained from these persons.

H. Basseches, Symposium Chairman

## ECS to Confer Three New Honorary Memberships

In recognition of distinguished service and for significant contributions to the science of electrochemistry, the Board of Directors, on recommendation of the Honors and Awards Committee, have unanimously elected three former Presidents as Honorary Members of The Electrochemical Society.





Robert M. Burns, Zurich, Switzerland; George W. Heise, Cleveland, Ohio; and Frank C. Mathers, Bloomington, Ind., have been chosen for this honor.

Certificates of Honorary Membership will be presented to these men



G. W. Heise

at the Annual Banquet on May 5 which will be held in conjunction with the Spring Meeting of the Society in Philadelphia.

The Banquet will be preceded by a Reception for the President of the Society and the newly elected Honorary Members.



R. M. Burns

# High Lights of the Meeting of the Board of Directors

(Held January 16, 1959, Society Headquarters, New York, N.Y.)

The regular midwinter meeting of the Board of Directors was held at Society Headquarters in New York on January 16, with President Sherlock Swann presiding and all officers and directors present either in person or represented by proxy.

#### **Communications from the President**

Report of Tellers of Election—The report of the Tellers of Election for officers of the Society for the year 1959-1960 was approved, and the following were declared elected to the office indicated: William C. Gardiner, President for one year; Frank L. LaQue, Vice-President for three years; Ivor E. Campbell, Secretary for three years.

Election of R. M. Burns as Honorary Member—President Swann presented a report from the Honors and Awards Committee recommending that Dr. Robert M. Burns be elected an Honorary Member of the Society. This recommendation was approved unanimously.

India Section Support from Asia Foundation—President Swann announced that appreciation has been expressed to The Asia Foundation for their financial support of members of the Society from the India Section for 1959.

Appointment of Interim Secretary of Society—President Swann reported that, in accordance with previous understanding, Dr. Linford had agreed to serve as Interim Secretary until the result of the election of the new Secretary had been determined by regular ballot of members of the Society. Now that it is known that Dr. Ivor E. Campbell has been elected as the new Secretary, President Swann announced his appointment as Interim Secretary until he takes office as the regularly elected Secretary at the time of our Spring Meeting in Philadelphia.

### **Report of the Treasurer**

Dr. L. I. Gilbertson presented the Financial Statement of Income and Expenses of the Society for the ninemonth period ending December 31, 1958. Receipts in the General Fund amounted to \$74,350.00, while expenses were \$80,058.00, leaving an excess of expenses over income in the General Fund of \$5707.00. However, it was reported that additional income which has been credited to the Society Reserve Fund amounted to \$6534.00, leaving net excess income over expenses of \$827.00. It is anticipated that receipts for the succeeding three-month period, terminating with the Society's fiscal year on March 31, will show a further improvement in these figures.

#### **Communications from the Secretary**

ASTM Request for Mailing List— Approval was granted to make available the Society's membership list to the American Society for Testing Materials for the sole purpose of publicizing their new book "Standards on Electron Tube Materials."

Report of Votes by Mail Ballot—It was reported that the following matters were voted on affirmatively by mail ballot by the members of the Board of Directors since the previous meeting:

(A) Approval of signing contract with Air Force Office of Scientific Research for financial support of our Symposium on Electrode Processes.

(B) Increase in budget appropriation of \$2000.00 for printing of the JOURNAL and an increase in salary appropriation of \$500.00 for additional editorial assistance. (C) Approval of appointment of Nominating Committee for 1959-1960.

(D) Approval of Corrosion and Electronics Divisions' joint symposium on the Chemistry of Metal and Semiconductor Surfaces; permission to solicit financial support from Government agencies; and an appropriation of \$1000.00 from Society funds.

(E) Approval of appointment of Dr. H. H. Uhlig as Chairman of the Publication Committee.

Bequest from A. T. Lincoln—It was reported that the last will and testament of Azariah T. Lincoln contained a bequest of approximately \$475.00 to the Society. The appreciation of the Society will be expressed to any remaining heirs. The Finance Committee was asked to make a recommendation with regard to the disposition of this money.

Special Symposia—The Secretary called attention to three special symposia being sponsored by Divisions of our Society at our 1959 meetings as follows:

(A) "Electrode Processes" symposium at Philadelphia Spring Meeting, sponsored by the Theoretical Electrochemistry Division and Air Force Office of Scientific Research.

(B) "Liquid Dielectrics" symposium at our Philadelphia Spring Meeting, sponsored by the Electric Insulation Division and the National Science Foundation and Office of Naval Research.

(C) "The Chemistry of Metal and Semiconductor Surfaces" symposium, sponsored by the Corrosion and Electronics Divisions with the Office of Naval Research.

Philadelphia Spring Meeting 1959 —The Secretary reported that 40 technical sessions will be held at our 1959 Spring Meeting in Philadelphia

## Manuscripts and Abstracts for Fall 1959 Meeting

Papers are now being solicited for the Fall Meeting of the Society, to be held at the Deshler-Hilton Hotel in Columbus, Ohio, October 18, 19, 20, 21, and 22, 1959. Technical sessions probably will be scheduled on Batteries, Corrosion (including a joint Corrosion—Electronics-Semiconductors session), Electrodeposition (including symposia on "Electrodeposition from Organic Solvents" and "Electro- and Chemical-Polishing"), Electronics (Semiconductors), Electro-Organics, and Electrothermics and Metallurgy.

To be considered for this meeting, triplicate copies of abstracts (not exceeding 75 words in length) must be received at Society Headquarters, 1860 Broadway, New York 23, N. Y., not later than June 1, 1959. Please indicate on abstract for which Division's symposium the paper is to be scheduled, and underline the name of the author who will present the paper. Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

\* \* \*

The Spring 1960 Meeting will be held in Chicago, Ill., May 1, 2, 3, 4, and 5, 1960, at the Lasalle Hotel. Sessions will be announced in a later issue.
at which 203 papers will be presented. This will be the largest number of papers ever presented at any meeting of the Society.

Future Meetings—The Secretary advised that contacts will be made with the Pittsburgh and Ontario-Quebec Sections for the Spring Meeting in 1963 and the Spring Meeting in 1964, respectively.

## Report of Ways and Means Committee

Amendment to Bylaws—Article IX, Sections 1 and 2 of the Bylaws were amended to facilitate the appointment of members to the Personal Membership Committee.

Exhibits at Meetings—Dr. Schaefer, Chairman, reported that a majority of the members of the Ways and Means Committee approved of exhibits of an educational or scientific nature of interest to our members at meetings of the Society at the discretion of the local meeting committee, subject to proper arrangements being made with respect to administration.

#### **Finance Committee**

Philadelphia and Columbus Meeting Budgets—The Board of Directors approved the budgets submitted by the Philadelphia and Columbus Meeting Committees.

Society Budget for 1959-1960—The Society budget for the year 1959-1960 was approved as submitted by the Finance Committee. Anticipated income in the General Fund is noted as \$113,250.00, while expenses are budgeted at \$121,380.00. However, income being credited to the Society Reserve Fund is anticipated to be \$12,300.00, leaving a net excess income over expenses of \$4170.00.

Society Finances—It was reported that the Finance Committee had been giving special consideration to the necessity of providing for the future growth and development of the Society and to potential sources of income which would provide for future necessities. Like other societies, we are confronted with increasing demands for service to our members and higher operational costs. This matter will be a subject of further consideration at the next Board Meeting.

Appropriations for Special Symposia—Approval was given to the Finance Committee's recommendation that appropriations of \$1000.00 each for our three special symposia being held in 1959 be paid from monies available to the credit of the Society Reserve Fund.

Advance for "Modern Electroplating"—Approval was given for an initial advance for the second edition of "Modern Electroplating."

#### **Report of Publication Committee**

The Board approved of the publication of a monograph on "Mechanical Properties of Intermetallic Compounds," covering papers to be presented at the 1959 Spring Meeting in Philadelphia, sponsored by the Electrothermics and Metallurgy Division. Dr. Uhlig, Chairman of the Publication Committee, emphasized that all Divisions which contemplate publishing a monograph should suggest to the authors that original important contributions be first published in the JOURNAL. This would insure their being abstracted separately by several abstract journals both here and abroad.

Prize Essay Contest—The matter of reinstituting the Prize Essay Contest was considered, and will be studied further by the Publication Committee.

Journal Statistics—Dr. King, Editor of the JOURNAL, presented figures indicating that a greater number of papers are appearing in the JOURNAL each year and that the number being revised and reviewed is decreasing.

Publication Rights—The following statement of policy was approved by the Board: "Presentation of a paper at a technical meeting of the Society does not guarantee publication in the JOURNAL. However, all papers so presented become the property of The Electrochemical Society, and may not be published elsewhere, either in whole or in part, unless released on proper request to the Editor."

The Publication Committee was authorized to prepare a similar statement of policy, with respect to papers submitted for publication in the JOURNAL.

#### **Report of Membership Committee**

The report of the Membership Committee indicated that the Society had a net increase of 141 members for the year 1958.

#### **Becket Award Committee**

It was announced that the following will comprise the Becket Award Committee: E. M. Sherwood, three

## Notice to Members and Subscribers

(Re Changes of Address)

To insure receipt of each issue of the JOURNAL, please be sure to give us your old address, as well as your new one, when you move. Our records are filed by states and cities, not by individual names. The Post Office does not forward magazines. years; J. H. Westbrook, three years; L. H. Juel, two years; R. R. Rogers, two years; I. E. Campbell, one year; G. M. Butler, one year.

#### Council of Local Sections

It was reported that the Council of Local Sections is still studying the matter of division of surplus funds resulting from national meetings of the Society.

It was suggested that the Ways and Means Committee should consider the procedures followed in granting credits to Local Sections for new members secured by them during the year as prescribed by our Bylaws.

Robert K. Shannon, Executive Secretary

# **Division News**

#### **Electronics Division**

The Nominating Committee (A. L. Smith, Chairman; L. W. Evans, A. E. Middleton) has selected the following nominees for officers of the electronics Division during the 1959-1961 term (two years):

- Chairman—M. F. Quaely, Westinghouse Electric Corp., Bloomfield, N. J.
- Vice-Chairman (Luminescence)— J. S. Prener, General Electric Research Lab., Schenectady, N. Y.
- Vice-Chairman (Semiconductors)
   —P. H. Keck, Sylvania Electric Products Inc., Bayside, N. Y.
- Vice-Chairman (General Electronics)—A. E. Martin, McGraw-Hill Book Co., New York, N. Y.
- Secretary-Treasurer—A. E. Hardy, Radio Corp. of America, Lancaster, Pa.

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 Chairman 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 Philadelphia, May 3-7, 1959.

M. F. Quaely, Sec.-Treas.

#### Electrothermics and Metallurgy Division

The Nominating Committee (B. W. Gonser, Chairman; I. E. Campbell, A. C. Haskell) reports that the following have been nominated as candidates for officers of the Electrothermics and Metallurgy Division, to be elected during the Spring Meeting of the Society in Philadelphia, May 3-7, 1959:

- Chairman—G. M. Butler, Carborundum Co., Niagara Falls, N. Y.
- Vice-Chairman-J. H. Westbrook, General Electric Co., Schenectady, N. Y.
- Vice-Chairman—E. M. Sherwood, Battelle Memorial Institute, Columbus, Ohio.
- Secretary-Treasurer—L. H. Juel, Great Lakes Carbon Corp., Niagara Falls. N. Y.
- Members-at-Large-M. A. Steinberg, W. E. Kuhn, E. W. Johnson, L. M. Litz.

B. W. Gonser, Chairman Nominating Committee

# Section News

#### **Boston Section**

The 15th meeting of the Boston Section of the Society was held on Monday, January 19, 1959, at the Arthur D. Little Research Labs. at Acorn Park. Dr. Charles Jerome, senior engineer, Sylvania Electric Products Inc., spoke on recent developments in the Panelescent Lamp.

He gave a brief history of the development of electroluminescence leading up to a description of the present Panelescent Lamp. He demonstrated various applications in which this lamp is now being used, such as automotive dials, aircraft signs, highway signs, clock dials, digital displays, and telephone dials operated both on conventional electric supply lines and on transistorized power supplies. Dr. Jerome concluded his talk with a demonstration of memory devices and image convertors. These are modifications of the Panelescent Lamp still in the development stage.

The next meeting, planned for April 1, will feature Dr. Brattain of Bell Telephone Labs. in Murray Hill speaking on "Surfaces of Semiconductors." He had been scheduled for March.

#### R. A. Peak, Secretary-Treasurer

#### Chicago Section

The Chicago Section of The Electrochemical Society and the Armour Research Foundation of Chicago, Ill., are co-sponsoring a "Symposium on Corrosion Inhibitors, Theory, and Mechanism," to be held on May 7, 1959, at the Illinois Insitute of Technology. The program is as follows.

Introductory Remarks by C. E. Barthel "Molecular Structure and Corrosion Inhibition" by Norman Hackerman

- "The Role of Film Formation in Corrosion Inhibition" by Morris Cohen
- "Mapping Inhibitor Action" by H. T. Francis
- "Metallic Cations as Corrosion Inhibitors and Corrosion Activators" by Henry Leidheiser, Jr., and W. R. Buck, III
- "Observations on the Mechanism of Passivating Inhibitors" by Milton Stern
- "Electrochemical and Electrostatic Factors in Inhibition" by G. H. Cartledge

A \$5.00 registration fee will cover lunch and abstracts of the talks. Although advance registration is preferred, registration is also possible on the meeting date. Inquiries should be made to M. J. Jans, Conference Secretary, Armour Research Foundation, 10 W. 35 St., Chicago 16, Ill.

J. M. Miller, Secretary

#### Washington-Baltimore Section

The third regular meeting of the Washington-Baltimore Section was held December 18, 1958 at the National Bureau of Standards. The speaker was Dr. James H. Schulman, head of the Dielectrics Branch of the Naval Research Lab., who spoke on the topic "Applications of the Luminescence of Glass."

He pointed out that the luminescent properties of inorganic glasses have found virtually no application until recently. The successful use of the radiophotoluminescence of silveractivated glass for radiation measurement has prompted investigations of the luminescence of glass under optical, cathode-ray, x-ray and nuclear particle excitations. Interesting features uncovered by these investigations were discussed.

## Personals

John M. Blocher, Jr., Electrothermics and Metallurgy Editor for the JOURNAL, has been appointed chief of Battelle Memorial Institute's Div. of Inorganic Chemistry and Chemical Engineering, Columbus, Ohio. In his 12 years at the research center, Dr. Blocher has been closely associated with studies in fields including thermodynamics, high-purity metals, and vapor-deposited refractory coatings. His recent activities have included work with the carbide coating of graphite, production processes for high-purity silicon and high-purity chromium, and the thermodynamics of titanium and its halides.

Paul L. Howard has been named assistant vice-president in charge of technical field operations at Yardney Electric Corp., New York City. A well-known authority on storage batteries, Mr. Howard was formerly director of technical operations at Yardney, with which he has been associated since 1952. In his new post, he will coordinate technical relations with company customers and assist them in working out their battery requirements. Mr. Howard, who has worked in various capacities for the U. S. Navy, the Atomic Energy Commission, and the National Bureau of Standards, holds several patents in the battery field and is active in many professional societies.

Charles A. Escoffery, leading physical chemist and researcher on numerous semiconductor projects, recently was named military products manager by International Rectifier Corp., El Segundo, Calif. Formerly chief chemist, and later manager of military research, Dr. Escoffery headed various research teams concerned with rectifiers, photocells, and other semiconductor devices. He is the holder of 24 issued patents, as well as several currently pending.

Lahmer Lynds has left the American Potash & Chemical Corp., Los Angeles, Calif., to join Atomics International as a research chemist in the solid-state compounds group.

**Thomas E. Harr** has transferred from General Electric's specialty Electronic Components Dept. in Auburn, N. Y., to the company's Advanced Electronics Center in Ithaca, N. Y.

**Russell A. Lindberg** has accepted a position as research engineer with the Boeing Aircraft Co., Seattle Div., Seattle, Wash. Formerly he was a metallurgist at the Naval Research Lab., Washington, D. C.

Arthur M. Wilson, a graduate of Northwestern University, and formerly a member of the Society's Chicago Section, is now on the faculty of the Chemistry Dept. at Wayne State University, and is affiliated with the Detroit Section.

#### JOURNAL ELECTROCHEMICAL SOCIETY

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## Electronics Division Enlarged Abstracts, Spring 1959

The Electronics Division again will print an "Enlarged Abstracts" booklet containing 1000-word abstracts of papers to be presented before the Electronics Division's symposia on Luminescence, Semiconductors, Thermionic Cathodes, and Electroluminescent Devices at the Philadelphia Meeting of The Electrochemical Society, May 3-7, 1959.

The booklets are expected to be ready for distribution sometime during the first two weeks of April.

The price will be \$3.50 per copy, with a discount of \$1.00 per copy for orders accompanied by payment and requiring no invoicing. This is by action of the Executive Committee of the Electronics Division. Note that orders requiring invoicing will be charged the full price even though payment accompanies order.

Checks should be made payable to: Electronics Division, The Electrochemical Society, and should be sent to

> Martin F. Quaely c/o Westinghouse Electric Corp.

Lamp Div., Research Dept. Bloomfield, N. J.

Extra copies, if any, will be on sale at the convention in Philadelphia.

\* \* \*

#### Theoretical Division Extended Abstracts, Spring 1959

The Theoretical Electrochemistry Division will print Extended Abstracts of the papers to be presented before the Symposium on Electrode Processes, sponsored jointly by The Electrochemical Society and the Air Force Office of Scientific Research of the Air Research and Development Command, and the papers to be presented at the General Session, at the Philadelphia Meeting of the Society, May 3-7, 1959.

The Extended Abstracts will be available at \$3.00 each about April 1, 1959 from

> Dr. Ralph Roberts 3308 Camalier Drive Washington 15, D. C.

**Everett L. Henderson** is the new head of the Chemistry Dept. at the University of Detroit, and a new member of the Detroit Section of the Society.

Norman P. Sweeny has left Indiana University, Bloomington, and has taken a position as research chemist with the Organic Section, Central Research Dept., Minnesota Mining & Manufacturing Co., St. Paul, Minn.

**Karl S. Willson** recently resigned his position with the Mallory Battery Co. to join the Chemical Research Staff of the Lubrizol Corp., Wickliffe, Ohio.

**Robert Yates,** formerly with the Dow Chemical Co., Freeport, Texas, is now with the Aerojet General Corp., Azusa, Calif.

William C. Zeek has transferred from Ray-O-Vac Co., Madison, Wis., to the Research Center, Electric Storage Battery Co., Yardley, Pa.

Malcolm McLoud has joined the Evans Products Co. of Plymouth, Mich., as sales manager for battery separators. In his new post, Mr. Mc-Loud will have charge of marketing the company's Evanite battery separators to the storage battery industry. Mr. McLoud comes to Evans from the U. S. Rubber Co., where he served since 1952 as assistant sales manager, battery separators.

I. S. Hirschhorn has been advanced from general manager to vice-president and general manager of New Process Metals, Inc., Newark, N. J., a Ronson Corp. subsidiary. Mr. Hirschhorn joined New Process Metals in 1949 as technical director, and was named general manager in 1950. He has authored numerous papers in the fields of rare earth metals and alloys, electronics, rocket propellants, and getters.

#### Van Winkle Todd

Van Winkle Todd, chairman of the Board of Directors of Hanson-Van Winkle-Munning Co., Matawan, N. J., died suddenly on January 15, 1959 at Monmouth Medical Center, Long Branch, N. J. He was 66 years old.

Mr. Todd was born in Newark, N. J., the son of the late Edmund N. and Anna Van Winkle Todd, and the grandson of the late Abraham Van Winkle, founder and president of The Hanson & Van Winkle Co. of Newark. Mr. Todd was president of this company at the time it merged, in 1927, with A. P. Munning & Co. of Matawan. He was president of the Hanson-Van Winkle-Munning Co., producers and distributors of supplies and equipment for the electroplating, anodizing, and metal finishing industries, from 1927 to 1948, and chairman of its Board of Directors from 1948 until his death.

Mr. Todd was graduated from Lawrenceville School in 1911, and was a member of the Princeton University Class of 1915. He served in World War I as First Lieutenant of the 103rd Aerial Squadron and saw service in France.

He was a member of The Electrochemical Society, which he joined in 1924; the American Electroplaters' Society; the Essex Club, Newark; Princeton and Whitehall Clubs, New York City; and the American Legion.

#### David C. Grahame

David Caldwell Grahame, professor of chemistry at Amherst College, Amherst, Mass., died of a heart attack in London on December 11, 1958, at the age of 46. He was returning from Aberdeen University, where he had given a lecture, to the University of Bristol, where he and his family were spending the academic year. He was the holder of a Guggenheim fellowship.

Professor Grahame was born in St. Paul, Minn., on April 21, 1912. He received the bachelor's degree in chemical engineering at the University of Minnesota in 1935, and the Ph.D. degree in physical chemistry at the University of California at Berkeley in 1937. He was an instructor in chemistry at Berkeley from 1937 to 1939, when he went to Amherst, becoming assistant professor in 1942, associate professor in 1947, and professor in 1953. He received an honorary M.A. degree from Amherst in 1953. He also was a member of the staff of the M.I.T. Radiation Lab. in 1945, and taught at Harvard in the summer of 1948.

His scientific work was largely in the field of electrochemistry. He published a total of 55 papers, including a large summary in *Chemical Reviews* of the work on the electrical double layer. Several of these papers appeared in the JOURNAL. He took an active part in several symposia arranged by the Theoretical Electrochemistry Division of The Electrochemical Society. His work at Amherst was supported by extensive grants from the Research Corp. and the Office of Naval Research.

Professor Grahame was an inspiring teacher of physical chemistry, and a number of chemists in this field received their start with him at Amherst. He served as secretarytreasurer of the Div, of Physical and Inorganic Chemistry and was secretary-treasurer of the Div. of Physical Chemistry of the American Chemical Society.

# News Items

#### **New Sustaining Member**

Philco Corp., Philadelphia, Pa., recently became a Sustaining Member of The Electrochemical Society.

#### **Bequest to ECS**

Azariah T. Lincoln, Professor Emeritus at Carleton College in Northfield, Minn., who died in September 1958, left a bequest of onesixtieth of his estate to The Electrochemical Society. The Society acknowledges this bequest with sincere appreciation. Professor Lincoln had been a member of the Society since 1902. He was elevated to Emeritus Membership in 1940.

#### H. H. Uhlig to Direct Summer Course in Corrosion at M.I.T.

A one-week intensive course in fundamentals of corrosion reactions and corrosion control will be offered at M.I.T. on June 22-26, 1959, inclusive. The course is designed for those who have had previous instruction in corrosion, such as is provided by various short courses sponsored by the National Association of Corrosion Engineers, or who have had continued contact with corrosion problems in practice, and who wish to enlarge their understanding of fundamentals. The lectures will emphasize reaction mechanisms, and interpretation of laboratory and field measurements from the standpoint of modern electrochemical and metallurgical concepts. Solutions of illustrative problems, and a quantitative approach to corrosion problems, will be presented. Lecture table demonstrations will be shown.

Lectures will cover the meaning and interpretation of electrode potentials and polarization measurements; calculation of corrosion rates from polarization data; passivity in metals and alloys; theory of cathodic protection and suitable criteria of complete protection; metallurgical factors affecting corrosion, in particular stress corrosion cracking and corrosion fatigue; mechanisms of corrosion inhibitors and their proper application; and mechanisms of oxidation and tarnish. A portion of each day will be set aside for questions and answers regarding application of principles to practice situations. Students should have previous acquaintance with elementary physical chemistry.

Lecturers will include Professor Norman Hackerman, head of the Dept. of Chemistry, University of Texas; Professor Bruce Chalmers, Gordan McKay Professor of Metallurgy, Div. of Engineering and Applied Physics, Harvard University; and Dr. Milton Stern, Metals Research Labs., Niagara Falls, N. Y. In charge of the course is Professor H. H. Uhlig, Corrosion Lab., M.I.T. Inquiries should be addressed to Professor James M. Austin, Director of Summer Session, Massachusetts Institute of Technology, Cambridge 39, Mass.

#### Thirteenth Annual Power Sources Conference

The Thirteenth Annual Power Sources Conference will be held on Tuesday, Wednesday, and Thursday, April 28-30, 1959, at the Shelburne Hotel, Atlantic City, N. J. This year the scope of the Conference has been expanded to cover all types of electrical power sources, in addition to presenting progress on the results of the battery research and development program.

Attendance at the Conference is by invitation only. Persons who wish to attend may make the necessary arrangements by writing direct to the Power Sources Div., U. S. Army Signal Research and Development Lab., Fort Monmouth, N. J.

Preliminary Program Registration—April 27-30 Space Power—April 28 Nuclear Energy Sources—April 28 Thermal Energy Conversion— April 28 Solar Energy Sources—April 28 Secondary Batteries—April 29 Comparison of Energy Conversion Systems—April 29 Fuel Cell Batteries—April 29 Primary Batteries—April 30 High-Rate Batteries—April 30 Cocktail Party—April 28 Banquet—April 28.

#### Symposium on Corrosion Inhibitors to be Held in May

Research in the field of corrosion inhibitors will be discussed at a meeting to be held in Chicago, Ill., on May 7, 1959, under the sponsorship of the Armour Research Foundation of Illinois Institute of Technology and the Chicago Section of The Electrochemical Society. The meeting entitled "Symposium on Corrosion Inhibitors" will be devoted to consideration of basic studies concerned with the theory and mechanism of inhibitory processes, according to Jacob Miller, associate electrochemist, Metals Research Dept., Armour Research Foundation.

Miller and Ernest L. Koehler, director, Electrochemical Metallurgy Lab., Continental Can Co., are the symposium chairmen.

Inquiries concerning the meeting should be sent to M. J. Jans, Armour Research Foundation, 10 W. 35 St., Chicago 16, Ill.

#### International Conference on Semiconductor Physics in Prague, 1960

The Czechoslovak Academy of Sciences is organizing the International Conference on Semiconductor Physics which will be held in Prague from August 29 to September 2, 1960, under the auspices of the International Union for Pure and Applied Physics, and which will continue the series of Conferences held in Reading, 1950; Amsterdam, 1954; Garmisch-Partenkirchen, 1956; and Rochester, 1958.

The Secretary of the Organization Committee is Dr. Milos Matyás, Institute of Technical Physics, Prague 5, Cukrovarnická 10, Czechoslovakia.

#### Metallurgical Society Announces Papers for Semiconductors Conference in Boston

The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers has announced a technical conference on "Properties of Elemental and Compound Semiconductors," to be held in the Statler Hotel, Boston, Mass., August 31 to September 2, 1959. Sessions will be divided between invited and contributed papers.

The invited session on Elemental Semiconductors will include a panel discussion of the "Role of Dislocations in Device Properties." Among the participants will be C. Mueller, Radio Corp. of America; A. E. Blakeslee, Bell Telephone Labs.; and W. C. Dash, General Electric Co.

Also included in this session will be papers on "Dislocations in Semiconductors," by W. C. Dash; "Semiconductor Surfaces and Films," by M. M. Attala; and "Defect Interactions in Semiconductors," by Howard Reiss, Bell Telephone Labs.

A second invited session, devoted to properties of compound semiconductors, will bring forward papers on "Stoichiometry in Compound

The conference will be sponsored by the Semiconductors Committee of the Institute of Metals Div. of The Metallurgical Society.

#### Mervin J. Kelly Award Established

Bell Telephone Labs., Inc., and the American Institute of Electrical Engineers have announced the establishment of an award for achievement in the field of telecommunications, to be known as the Mervin J. Kelly Award.

The award is named in honor of Dr. Kelly, formerly president and now chairman of the board of Bell Labs., who retired on March 1 after 41 years of scientific and administrative service with the Bell Telephone System. Dr. Kelly is a Fellow of the American Institute of Electrical Engineers and has been active in Institute affairs for 33 years. He is internationally recognized as one of the world's leading scientists and research administrators, whose distinguished achievements have played a large part in the advance of telecommunications during the past four decades.

The Kelly Award will be made annually by the American Institute of Electrical Engineers to an individual who has made an outstanding contribution to the advancement of the art of telecommunications. The prize will consist of a bronze medal, a cash stipend of \$1000.00, and a certificate. The first award will be made by the American Institute of Electrical Engineers in 1960. The award is being sponsored by Bell Labs. but will be administered solely by the Institute.

#### First National Youth Conference on Atom Announced

A national Youth Conference on the Atom, the first such meeting of high school science students and teachers to discuss the peaceful uses of nuclear energy, will be held in Atlantic City, N. J., April 30-May 1, 1959.

Approximately 500 junior and senior high school science students and teachers will be sponsored in attendance at the conference by 60 or more electric utility companies throughout the country.





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Organizations cooperating in the conference include the American Association for the Advancement of Science, Atomic Industrial Forum, Future Scientists of America Foundation, National Science Foundation, National Science Teachers Association, and Science Clubs of America.

The two-day conference at Atlantic City's Claridge Hotel is being held, sponsors said, to inform students and teachers about the many uses of the peacetime atom, and to help advance interest in the study of science.

The students and teachers attending the conference will tour the Atomic Energy Commission's new 1959 version of its major "Atoms for Peace" exhibit, which will visit Atlantic City during the week of the conference as the first stop in a nation-wide tour. In addition, the Atomic Energy Commission and more than 25 other organizations will have exhibits at the conference site.

Students who will attend the conference will be chosen in cooperation with local school authorities in a variety of ways, ranging from selection by school principals to essay contests and special examinations. They will be selected for their excellence and interest in science, particularly physics.

#### ISA Sponsoring Translation of Four Soviet Journals

The Instrument Society of America, under a grant-in-aid from the National Science Foundation, is sponsoring complete English translations of four leading Soviet journals. The ISA "Soviet Instrumentation and Control Translation Series" is the continuation of a program initiated last year by the Massachusetts Institute of Technology. Undertaken as a service to American science and industry, it affords an excellent means for U.S. scientists and engineers to become better informed of the latest developments in the field of Soviet instrumentation

The four translated publications include the important Soviet journals Measurement Techniques (Izmeritel' nava Tekhnika), Instruments and Experimental Techniques (Pribory i Tekhnika Eksperimata), Automation and Remote Control (Avtomatika i Telemekhanika), and Industrial Laboratory (Zavodskaya Laboratoriya). All are available through the Instrument Society of America at a very low subscription rate ranging in price from \$20.00 to \$35.00 per annual subscription. Special rates are offered libraries of nonprofit academic institutions and for a combined order to all four journals. Translations and printing are handled by Consultants Bureau, Inc., of New York.

For subscription or additional information on Russian journals, write Instrument Society of America, 313 Sixth Ave., Pittsburgh 22, Pa.

#### **ECS Volumes Available**

A set of TRANSACTIONS of The Electrochemical Society from 1924 to 1945, comprising 43 volumes, is available at a reasonable price. Anyone interested in obtaining them should contact Mr. G. D. Mallory, Technical Adviser, Dept. of Trade and Commerce, Ottawa, Ont., Canada.

#### Production Begun at AP&CC Sodium Chlorate Plant

American Potash & Chemical Corp.'s new \$4,300,000 sodium chlorate plant at Aberdeen, Miss., went on stream recently. Delivery of finished product was expected by mid-February after the usual tuneup period.

The new plant, designed for an initial production of 15,000 tons of sodium chlorate per year, was constructed primarily to supply chemicals to the rapidly growing southern pulp and paper industry for bleaching. It also is used in weed killers and cotton defoliants.

Production at the Aberdeen plant, combined with sodium chlorate output at the Henderson, Nev., plant of American Potash & Chemical Corp., will total approximately 40,000 tons per year, about 45% of current domestic consumption, and will make AP&CC the largest producer in the United States.

Aberdeen plans include provisions to expand sodium chlorate production facilities to meet future demand or to manufacture oxidizers, and American Potash & Chemical Corp. has the only existing large-scale facility for manufacturing ammonium perchlorate at its Henderson, Nev., plant.

#### Expansion of Transistor Manufacturing Operations Announced by RCA

Plans for the expanded production of high-performance transistors used for specialized applications in computers as well as industrial and military electronic equipment were disclosed recently by the RCA Semiconductor and Materials Div., Somerville, N. J.

Simultaneously, appointment was announced of John M. Spooner as plant manager of the Findlay, Ohio, plant, and Clifford H. Lane as plant manager at Somerville.

The Somerville plant, headquarters of the RCA Semiconductor and Materials Div., is being expanded from 177,000 square feet to 267,000 square feet. At the same time, the company's modern 132,000-square foot plant at Findlay, Ohio, is being converted to a transistor manufacturing facility from its former operation as a television components plant.

These moves are part of the division's plan to expand its manufacture of silicon and germanium transistors and rectifiers for computer, industrial, and military applications, as well as for entertainment equipment.

# Announcements from Publishers

- "Isotopes: A Bibliography of United States Research and Application 1955-1957," including an author index and a key to journal abbreviations. AEC Report TID-3076,\* 267 pages; \$2.25.
- "Temperature Dependence of Tafel Slope in the Formation of Very Thin Anodic Oxide Films on Niobium," 1957. AEC Report AECU-3769,\* 10 pages; 50 cents.
- "Hydrogen and Oxygen Isotopes Applied to the Study of Water-Metal Reactions: Exchange of D<sub>2</sub>018 with Alpha Alumina Monohydrate," Aug. 1958. AEC Report ANL-5889,\* 15 pages; 50 cents.
- "Polarography of Europium and Ytterbium," Aug. 1958. AEC Report APEX-405,\* 19 pages; 75 cents.
- "Electroplating of Tapered Silver Deposits on Stainless Steel and Inconel Tubes for a High-Capacity Mercury-Column Rheostat," Jan. 1958. AEC Report LAMS-2206,\* 18 pages; 75 cents.
- "Electrochemical Studies in Cyclic Esters: (Thesis)," July 1958. AEC Report UCRL-8381,\* 77 pages; \$2.00.
- "Gas-Handling System for the Processing Refabrication Experiment," Aug. 1958. AEC Report NAA-SR-2309,\* 79 pages; \$2.00.
- "Adsorption of Ruthenium by Ion Exchange Resins," June 1958.
- Order from Office of Technical Services,
   U. S. Dept. of Commerce, Washington 25,
   D. C.

AEC Report DP-291,\* 16 pages; 50 cents.

- "Complex Metal Halides in Fused Alkali Nitrates," Dec. 1957. AEC Report ISC-943,\* 75 pages; \$2.25.
- "Casting Uranium-5 w/o Zirconium-1.5 w/o Niobium Alloys into Zirconium and Zircaloy-2C Containers," July 1958. AEC Report ANL-5442.\* 49 pages; \$1.50.
- "Effects of Irradiation on Some Uranium-Plutonium Alloys: Final Report," June 1958. AEC Report ANL-5706,\* 23 pages; 75 cents.
- "Properties and Handling Practices for Magnesium: A Literature Survey," March 1958. AEC Report ANL-5749,\* 132 pages; \$2.75.
- "Corrosion by Solutions Containing HNO<sub>3</sub>, HF, and Reducing Agents," May 1958. AEC Report DP-284,\* 24 pages; 75 cents.
- "Corrosion Product Activity in the Primary System of the Army Package Power Reactor," April 1958. AEC Report APAE-29,\* 70 pages; \$2.00.
- "Electronic Component Parts Research for 500°C Operation;" M. E. Goldberg and H. G. Hamre, Armour Research Foundation, for Wright Air Development Center, U. S. Air Force, Feb. 1958. Report PB 131815,\* 110 pages; \$2.50.
- "Spectrographic Determination of Magnesium in Cast Iron," Springfield Armory, U. S. Army Ordnance Corps, June 1957. Report PB 131545,\* 11 pages; 50 cents.
- "The Change in Electrical Resistivity of Some High Polymers during Isothermal Polymerization," J. A. Aukward, R. W. Warfield, and M. C. Petree, U. S. Naval Ordnance Lab., Nov. 1956. Report PB 131582,\* 20 pages; 75 cents.
- "High Rate Discharge Characteristics of Lead-Acid Storage Batteries," C. B. Derricotte, Detroit Arsenal, Oct. 1956. Report PB 131498,\* 27 pages; 75 cents.
- "Research on Methods of Treating Cadmium Sulfide Elements," A. Carlson, W. Deshotels, J. M. Jost, and L. R. Shiozawa, Clevite Research Center, for Wright Air Development Center, U. S. Air Force, Nov. 1957. Report PB 131847,\* 58 pages; \$1.50.

• Order from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C.

- "The Effect of Corrosion and Growth on the Life of Cycling Lead-Acid Cells," J. J. Lander, A. C. Simon, and E. L. Jones, Naval Research Lab., March 1958. Report PB 131588,\* 18 pages; 50 cents.
- "Investigations and Measurements of Properties of Single-Crystal Silicon: Final Report," A. C. Beer and others, Battelle Memorial Institute, for Air Research and Development Command, U. S. Air Force, Sept. 1957. Report PB 131586,\* 19 pages; 50 cents.
- "Nonmetallic Ferromagnetic Materials and Devices: Frequency Dependent Delay Line; Magnetostrictive Filters; Low-Loss, 10Mc-50Mc Ferrite Material," J. W. Brouillette, H. W. Katz, L. Marcus, G. G. Palmer, O. N. Salmon, and N. Schwartz, General Electric Co., for Wright Air Development Center, U. S. Air Force, March 1958. Report PB 151021,\* 67 pages; \$1.50.
- "Effect of Neutron Irradiation on the Curie Temperature of a Variety of Ferrites," E. I. Salkovitz, G. C. Bailey, A. I. Schindler, Naval Research Lab., July 1958. Report PB 131838,\* 6 pages; 50 cents.

# **Book Reviews**

Industrial Carbon and Graphite, Papers read at the Conference held in London, September 24-26, 1957, with the discussions that followed, Society of Chemical Industry, London. Published by Macmillan Co., New York City, 1958. 630 pages; \$25.75.

The papers and discussions published in this compendium are divided into six Sessions: I. Introduction and Physical Properties; II(a) The Manufacture of Carbon and Graphite, (b) The Crystal Structure of Carbon and Graphite; III. Surface Chemical Properties and Reactivity; IV. Electrical Behavior and Applications; V. Graphite in the Nuclear Power Industry; VI. Mechanical, Chemical, and Metallurgical Applications.

Of the 67 papers, 63 are given in English, 4 in French. Topics covered in the 11 papers given in Session IV are: Surface Disintegration of Carbon Electrodes; Distribution of Electrode Consumption in an Electric Arc Furnace; Investigation into the Electric Contact Properties of Carbon; Some Electrical Properties of Carbon Contacts; Recent Developments in the Use of Carbon for Cur-

# ELECTROCHEMISTS PHYSICAL CHEMISTS B.S. – M.S. – PH. D.

POSITIONS OPEN IN BASIC RESEARCH AND DEVELOPMENT WORK ON NEW BATTERY TYPES. EXPERIENCE OF 3 TO 5 YEARS DESIRED ON OTHER THAN LEAD-ACID BATTERIES.

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POSITIONS OPEN FOR MEN EXPERIENCED IN NICKEL-CADMIUM AND/OR SILVER-ZINC BATTERY DEVELOPMENT.

All inquiries will be held confidential. Address inquiries with résumé to

M. J. Cavanaugh, Director of Salaried Personnel Delco-Remy Division, General Motors Corp. Anderson, Indiana Dept. 135A rent Collection; Carbone et Contact Glissant; Electrical Conductivity Characteristics of Carbon Black; Copper-Graphite Materials; The Use of Carbon in High-Temperature Laboratory Furnaces; Properties of Carbon Blacks as Affecting their Use in Resistors; The Design of High-Temperature Furnaces Using Graphite Elements.

Editing and typography are excellent. Discussions which follow the papers are generally very illuminating. The book constitutes an especially valuable collection of up-todate information on European (including Russian) work in this important field.

#### Amos Turk

**Emulsions—Theory and Practice**, by Paul Becher. Published by Reinhold Publishing Corp., New York City, 1957. ix + 382 pages; \$12.50. The author has produced a readable and compact book about the very diffuse and complex field of emulsion theory and practice. It provides a basis for the beginner and a review for the active worker in the field.

The theory is covered by a review of the physical chemical basis, surface activity, physical properties of emulsions, and theories of emulsion stability. The chapter on physical properties correlates well with a subsequent chapter on methods for testing of emulsions. The practical or experimental side is covered in chapters on methods for testing of emulsions; on the chemistry of emulsifying agents, emphasizing classification; on techniques of emulsification, emulsion applications, and demulsification. A fairly complete table of commercial emulsifiers with their chemical names rounds out the book.

#### M. M. Fishman

1957 Fourth National Symposium on Vacuum Technology Transactions. Edited by W. G. Matheson. Published by Pergamon Press, New York City, 1958. X + 176 pages; \$12.50.

This volume contains the texts of 28 papers presented at the Fourth National Symposium of the American Vacuum Society, Inc., held in Boston, October 9, 10, and 11, 1957. The papers are given in three sections: Scientific Basis of Vacuum Techniques and their Applications to Scientific and Applied Research; Methods and Techniques for Obtaining and Measuring High Vacuum and Ultra-High Vacuum—Industrial Applications; Industrial Applications. The topics covered include applications of vacuum techniques to special research problems such as metal films, large and small ultra-high vacuum systems, vacuum metallizing, vacuum metallurgy, systems for nuclear particle accelerators, and vacuum drying.

Of this large number of papers, those on modern developments in both large and small systems would particularly interest the research worker. The little understood field of ion pumping is represented with a paper by G. Reich and H. G. Nöller, "Production of Very Low Pressures with Getter-Ion Pumps." A titanium film ion pump was used to evacuate a system containing an omegatron mass spectrometer for residual gas examination. They found that it was necessary to exclude organic vapors from the system if pressures in the ultra-high vacuum range were to be reached.

J. R. Ullman in "A Large Metal System Permitting Low Base Pressures" describes a stainless steel system of speed 25 l per sec and ultimate pressure of a few times  $10^{-10}$  mm of Hg.

Two papers related to nuclear physics contain information that could be beneficial to other types of work requiring pressures less than  $10^{-5}$  mm of Hg. They are those of R. N. Edwards and J. F. Lawyer, "Design Criteria for Accelerator Vacuum Systems," and of M. Auwaerter, "High Vacuum Techniques for Nuclear Physics." The effects of poor vacuum on beam current and on electrical breakdown are treated in some detail.

Certain problems of technique

# Conn produces the "heart" of good tone quality by electrodeposition, with "Plus-4" Copper Anodes

In a cornet or trumpet, good tone and easy playing depend largely on the inside shape and finish of the tone chamber (mouthpipe).

Aiming at perfection, C. G. Conn, Ltd., famous maker of band instruments, turned to forming these critical parts by electrodeposition of copper on stainless steel mandrels. The deposited copper conforms perfectly to the precision mandrel—providing the exact taper and dimensions every time. It also gives the smooth mirror-like inside surface that prevents acoustical losses. Even minor irregularities caused by forming sheet metal or tube can muffle, distort, or rattle the tone.

Using "Plus-4" Phosphorized Copper Anodes in its acid-copper electroplating tanks, Conn has found it gets the smooth, dense deposit it needs. The build-up of metal is fast and uniform; "Plus-4" Anodes' extra "throwing power" being of particular value with the tubular shapes. There are few nodules, which minimizes finishing of the outside surface. And tank maintenance is simplified.

Conn also forms the bells used in cornets, trumpets, and trombones electrolytically. This gives still further control in the precision of the entire inside tone columns of its instruments – for increased resonance and live, powerful tone.

WRITE FOR INFORMATION on how you can obtain a test quantity of "Plus-4" Anodes to supply one tank. Address: The American Brass Company, Waterbury 20, Conn. In Canada: Anaconda American Brass Ltd., New Toronto, Ont.

Top Right: Conn Electro-D Tone Chamber (mouthpipe) cut away to illustrate the "micro finish" interior surface. Chamber and mouthpiece receptacle are formed in one piece by electradeposition; were previously two pieces soldered together. (Patent pending.)

**Bottom Right:** Electro-D Bell, also formed by electrodeposition.

**ANACONDA** "PLUS-4" ANODES Phosphorized Copper Made By The American Brass Company might be simplified by further application of the methods presented by N. Milleron. In the "Utilization of the Surface Tension of Liquid Metals in Making High-Vacuum Seals," he shows that liquid metal alloys of Ga, In, and Sn have negligible vapor pressures even at 400°C, and can be made to wet W, Mo, Ta, glass, quartz, and ceramics. Motion seals, valves, and joints thus can be made using such alloys. Design data is given.

Some results on the evaporation patterns of gold and chromium from sources commonly used in the laboratory is reported by L. E. Preuss and C. E. Alt in "The Evaporation Mode of Certain Vacuum Metal Distillation Source Configurations." A pinhole camera technique with radioisotope tagged metals and autoradiography gave them a very sensitive way of studying evaporation from straight wire, helix, and "Vee" filament sources. Several photographs show the results.

Metallizing is further discussed in two more highly applied papers. The problems of evaporating onto flexible substrates, of crucibles, of substrate heating, and of geometry are considered by P. J. Clough in the "Metallizing of Flexible Substrates." T. J. LaBounty in "Vacuum Metallizing on Plastics" describes the various plastics commonly encountered in metallizing, with the effects on results of plasticizers, leaks, and dust.

Since the range of subjects covered in this book is very large, only a few of the papers are likely to be of great interest to any one person. Those papers which have been singled out for mention above ignore



the material on vacuum metallurgy, partly because the four papers on that subject tend to be very broad surveys. The papers have references, but often more would be desired by the reader who would like to use this book to help familiarize himself with a new field. It does fulfill a useful purpose in showing the activity in the rapidly changing field of modern vacuum technique.

R. N. Peacock

# Literature from Industry

Answers on Electron Microscope Questions. A new 12-page Norelco booklet, titled "Questions and Answers on Electron Microscopes," is available from the Instruments Div., Philips Electronics, Inc., 750 So. Fulton Ave., Mount Vernon, N. Y. Compiled from actual queries asked in the field and at Norelco Microscope School sessions, the booklet discusses magnification, resolution, specimen preparation, and fields of application. Shadow casting, electron diffraction, camera work, stereo techniques, astigmatism correction, lens details, beam wobbler, through-focus control, and many other technical matters are covered also.

Cobalt. The Cobalt Information Center announces the availability of a new illustrated quarterly review, Cobalt. This journal (published both in French and English) will present articles of general interest, technical articles on the varied uses of cobalt and its alloys, reports on cobalt research and development projects sponsored by the Centre d'Information du Cobalt, abstracts of current U. S. and European literature on cobalt, and news items of interest to cobalt users. This new review will replace the monthly publication "Literature Abstract Bulletin." which has been discontinued.

The first issue of Cobalt features technical articles on "The Uses of Cobalt" and "High-Temperature Alloys." "The Uses of Cobalt" includes information on world production and U. S. consumption, a historical survey of early uses, uses in numerous cobalt alloys, uses of cobalt compounds, radioactive cobalt, electroplated cobalt, and cobalt in biochemical sciences. "High-Temperature Alloys" presents applications and compositions of heat-resistant alloys, properties of superalloys, and future prospects. A section containThe Office of Naval Research, as the central research organization of the Navy Department, sponsors broad programs of basic and applied scientific research in university and other laboratories. The services of outstanding research scientists are employed to plan, organize, and direct major contract research programs in their fields.

The Metallurgy Branch of the Office of Naval Research offers excellent opportunities for qualified research scientists in the fields indicated below. Salaries range from \$10,130 to \$12,770 depending upon qualifications.

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(Solid State emphasis)—Imperfections in solids, physics of metals, deformation and fracture phase transformations, chemistry and physics of surfaces and interfaces.

#### CERAMIST or SOLID STATE CHEMIST

Ceramics and inorganic nonmetallic solids including defect structure and structure-sensitive properties, solid-state reactions, mechanical behavior; semi-conducting materials for energy conversion systems; ferroelectric, dielectric, ferromagnetic and special materials.

These positions are for duty in Washington, D. C., and will be filled in accordance with applicable civil service procedures. University scientists on sabbatical leave considered.

Applicants are invited to send their qualifications and inquiries to Director, Civilian Personnel and Services Division.



**Office of Naval Research** 

Room 1070, T-3 Bldg., 17th & Constitution Washington 25, D.C. ing 68 abstracts from the current technical literature is included also. Interested persons can obtain this issue by addressing requests on company letterhead to the Cobalt Information Center, c/o Battelle Memorial Institute, 505 King Ave., Columbus 1, Ohio. Requests outside the Americas should be directed to Centre d'Information du Cobalt, 35, rue des Colonies, Brussels, Belgium.

**Physical Properties Booklet.** An attractive new 1959 edition of the comprehensive "Physical Properties" booklet has been published by Union Carbide Chemicals Co., Div. of Union Carbide Corp. This booklet has come to be regarded as a reference work on physical properties of a wide variety of organic chemicals by purchasing agents, chemists, engineers, and teachers.

The 1959 edition covers more than 400 organic chemicals, with tabulations of carefully determined physical properties and brief descriptions of fields of application. There are 57 products covered in the new edition for the first time, including "Niax" polyethers and "Polyox" water-soluble resins. Additional physical property data are available on "Cellosize" hydroxyethyl cellulose.

In addition to the inclusion of new commercial products, a center spread features "new chemicals"—those materials available in development quantities today, many of which will find their way into the 1960 edition of the "Physical Properties" booklet as full-fledged commercial chemicals.

For the purchasing agent, information on shipping of commercial material has been added. The 28-page booklet opens with a table of contents and features the use of color to draw attention to sections of interest.

Write Union Carbide Chemicals Co., Div. of Union Carbide Corp., 30 E. 42 St., New York 17, N. Y.

Bibliography on Silicon Carbide. A limited number of a new comprehensive bibliography on silicon carbide has been compiled by Mr. K. M. Merz of the Research and Development Div. of the Carborundum Co. Prepared in response to numerous requests for information on silicon carbide, it is a 107-page listing of scientific literature on the subject. Authors are listed alphabetically. Subject keys are listed in the forefront and in the margins by each author listing.

Available while they ast at the Advertising Distribution Section, Carborundum Co., Niagara Falls, N. Y. **Booklet on "Hastelloy" Alloy C.** An alloy that has built a reputation as being one of the most universally corrosion-resistant alloys available is the subject of a newly printed, 16page booklet. This piece of technical literature combines the latest data pertaining to "Hastelloy" alloy C under one cover. Chemical, physical, and mechanical properties, along with a guide to corrosion resistance, are presented through the use of charts and graphs. Valuable data on the excellent high-temperature properties of alloy C are also included.

"Hastelloy" alloy C is a product of Haynes Stellite Co., Div. of Union Carbide Corp., Kokomo, Ind., from which copies of the booklet can be obtained.

# **New Products**

Zdansky-Lonza Pressure Electrolyzer. Highest purity industrial hydrogen and oxygen now can be economically produced here by means of pressure electrolysis. The process is made possible by availability of the Zdansky-Lonza Pressure Electrolyzer, developed by Lurgi of Frankfurt, West Germany, and offered exclusively throughout the United States and Canada by Winfield Equipment Co., Cleveland, Ohio.

Compared with earlier and conventional electrolyzers, which operate at atmospheric pressure, the Zdansky-Lonza unit is completely new in concept because of tremendously high pressure generated without use of compressors-30 atm gauge pressure on an industrial scale. Purity obtained is 99.9% for hydrogen and about 99.8% for oxygen. Thus, they are ready to use, or sell, at the end of this self-contained process. Important additional savings are realized by companies which have their own, or low-cost, power as only electricity and water are needed and heat is all but eliminated. Capacity range is 5000-25,000 ft' of hydrogen per hr.

Complete technical details are available from Winfield Equipment Co., 20950 Center Ridge Rd., Cleveland 16, Ohio.

**Recording Polarograph.** A new recording polarograph for laboratory use has been developed by E. H. Sargent & Co. This recording polarograph, called the Model XV, is designed with maximum simplicity of operation for the routine analyst. It

includes full facilities for application to every phase of conventional polarography with full-size recording and analytical accuracy at an economical price. The polarograph is flexible and adaptable to future accommodation of specialized techniques as they become useful. It permits direct alternate use as a recording potentiometer of 2.5 mv range.

For further information on the new Model XV polarograph, please address inquiries to E. H. Sargent & Co., Dept. RP, 4647 W. Foster Ave., Chicago 30, Ill.

Silicon-Rectifier Battery Chargers. A complete line of new siliconrectifier battery chargers, providing the most accurate voltage control available in chargers for stand-by batteries, has been introduced by Exide Industrial Div. of the Electric Storage Battery Co., Philadelphia. The new units are controlled by a high-quality magnetic amplifier with a sensing control circuit which automatically maintains the proper charging voltage at the battery terminals. The new chargers are for use with stationary batteries in electric utility service, in emergency power, emergency lighting, and in other floatcharge battery applications in which accurate charge control is essential.

Designed for floor, wall, or rack mounting—depending upon size—the new chargers come in 27 basic models, for use with batteries having from 11 to 62 cells. Both single- and three-phase units are available, having an output range of from 1 to 400 amp. Single-phase units can be operated at 115 or 230 v; three-phase units at 230 or 460 v.

Further information on the siliconrectifier chargers for stand-by batteries, other types of charging equipment, Exide industrial batteries, or complete battery-charger installations can be obtained by writing to Exide Industrial Div., Electric Storage Battery Co., Rising Sun and Adams Aves., Philadelphia 20, Pa.

## **Employment Situations**

#### **Positions Available**

Engineers (Aeronautical, Electrical, Electronic, Industrial, General, Mechanical, and Power Plant), Electronic Scientists, Metallurgists, Physicists, Technologists—Vacancies exist for professional personnel in the above positions. Starting salaries range from \$4490 per annum to \$10,130 per annum. The Naval Air Material Center is currently engaged in an extensive program of aeronautical research, development, experimentation, and test operations for the advancement of Naval aviation. Experimental work also is being conducted in the guided missile field. Personnel are needed for work on projects involving modification. overhauling, and testing of aeronautical equipment, materials, accessories, power plants, launching and arresting devices, and for modification and structural testing of aircraft. Also, for work involving the basic design of catapults, launchers, arresting gear and their component parts; test and development work at shore stations and on board U.S. Navy ships; evaluation of new equipment and establishment of performance parameters, and applied research on the many problems relevant to this field.

Interested persons should file an Application for Federal Employment, Standard Form 57, with the Industrial Relations Dept., Naval Air Material Center, Naval Base, Philadelphia 12, Pa. Applications may be obtained from the above address or information as to where they are available may be obtained from any first or second class post office.

Chemists, Physicists, Metallurgists —New R&D Lab. needs qualified personnel to handle projects in electrochemical, lead acid, and related areas. Latest equipment—fine working conditions—fringe benefits. Must relocate to Twin Cities. Send résumés to: T. W. Murphy, Personnel Dept., Gould-National Batteries, Inc., E. 1326 First National Bank Bldg., St. Paul 1, Minn.

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The Electrochemical Society

# INSTRUCTIONS TO AUTHORS OF PAPERS

Address all correspondence to the Editor, JOURNAL OF THE ELECTROCHEMICAL SOCI-ETY, 1860 BROADWAY, NEW YORK 23, N. Y.

Manuscripts submitted for publication should be in triplicate to expedite review. They should be typewritten, double-spaced, with  $2\frac{1}{2}-4$  cm (1-1 $\frac{1}{2}$  in.) margins.

*Title* should be brief, followed by the author's name and his business or university connection.

Abstract of about 100 words should state the scope of the paper and give a brief summary of results.



FORM

**Drawings** will be reduced to column width, 8.3 cm (3¼ in.), after reduction should have lettering at least 0.15 cm (1/16 in.) high. Original drawings in India ink on tracing cloth or white paper are preferred. Curves may be drawn on coordinate paper only if the paper is ruled in blue. All lettering must be of lettering-guide quality. See sample drawing on reverse page.

Photographs must be glossy prints and mounted flat.

**Captions** for all figures must be included on a separate sheet. Captions and figure numbers should not appear in the body of the figure.

**General**—Figures should be used only when necessary. Omit drawings or photographs of familiar equipment. Figures from other publications are to be used only when the publication is not readily available, and should always be accompanied with written permission for reprinting.

If more than a few symbols are used, these should be defined in a list at the end of the paper, for example:

 $a, b \ldots =$  empirical constants of Brown equation

- $f_i^* =$  fugacity of pure *i*th component, atm
- $D_* =$ bulk diffusion coefficient, cm<sup>2</sup>/sec

Literature and patent references should be listed at the end of the paper on a separate sheet, in the order in which they are cited. They should be given in the style adopted by *Chemical Abstracts*. For example:

- R. Freas, Trans. Electrochem. Soc., 40, 109 (1921).
  - H. T. S. Britton, "Hydrogen Ions," Vol 1, p. 309, D. Van Nostrand Co., New York (1943).
- H. F. Weiss (To Wood Conversion Co.), U. S. Pat. 1,695,445, Dec. 18, 1928.

Metric units should be used throughout but, where desirable, English units may be given in parentheses.

Corrosion rates in the metric system should preferably be expressed as milligrams per square decimeter per day (mdd), and in the English system as inches penetration per year (ipy).

In reporting electrode potentials, the sign of the standard  $Zn/Zn^{**}$  electrode potential should be taken as negative;  $Cu/Cu^{**}$  as positive.









Abbreviations should conform with the American Standards Association's list of "Abbreviations for Scientific and Engineering Terms."



Authors should be as brief as is consistent with clarity, and must omit all material which can be regarded as familiar to specialists in the particular field.

The use of proprietary names, trade-marks, and trade names should be avoided if possible. If used, these should be capitalized so that the owner's legal rights are not jeopardized.



Remarks: Line weight 2 is used for borders and zero lines. When several curves are shown, each may be numbered and described in the caption. Lettering shown is approximately 1/8 in. In plotting current or potential as ordinate, increasing negative values should go down.

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Compare treated vs untreated brass panels, After cleaning, panel on right was rinsed in Entek 45 rinse; panel on left, in standard hot water rinse. Then panels were exposed to 100% humidity at 100° F. jor 100 hours. Note how Entek 45 preserves "that jresh metal surface

From Enthonics research come Enthone Enteks, a new series of rinse water additives which coat metal surfaces with an "invisible shield" against the atmosphere. Entek 45 assures faster drving. eliminates water spots and provides lasting corrosion protection to all metals. Entek CU-55 prevents tarnishing and spotting out of copper and brass even under tropical humidity conditions.

By adding Entek 45 to your final hot water rinse, you can prevent white salt corrosion of zinc and aluminum, prevent yellowing of nickel plate, prevent tarnishing of copper and brass, prevent black spots on cadmium plate.

By treating copper and brass goods or copper or brass plated items with Entek CU-55 you can prevent tarnishing, green salt formation, spotting-out and pit corrosion under high humidity storage conditions.

Entek protection lasts for months, yet costs less than 11/2¢ per 100 sq. ft. to treat your parts, less than 1/2¢ per gallon to make up an Entek 45 solution!

Entek 45 produces an invisible, water-repellent organic film on the metal surface which sheds water rapidly and promotes stain-free drying. This same film acts as an invisible barrier between the metal and the moisture and oxygen in the air.

Entek CU-55 reacts with copper and copper alloys to form an invisible layer which has many times the corrosion resistance of bare copper and brass. Additionally, this layer has better solderability and improves adhesion of lacquers and enamels.

Write today for complete literature on both of these products to Enthone, Inc., 442 Elm Street, New Haven, Connecticut.





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