

JOURNAL OF THE

# Electrochemical Society

Vol. 105, No. 5

May 1958



แผนกฟิสิกส์ คณะวิทยาศาสตร์  
ภาควิชาฟิสิกส์ มหาวิทยาลัยศรีนครินทรวิโรฒ

M. I. T. Lincoln Laboratory  
APR 29 1958  
Received - Library



## Keeping Hooker Cells at their best

Making the best use of the remarkable efficiency of Hooker cells depends upon the skills of the men who operate them.

Also at work, with a skill all their own, are GLC ANODES, which are "custom made" to individual cell requirements.

**FREE** — This illustration of keeping cells at peak efficiency has been handsomely reproduced with no advertising text. We will be pleased to send you one of these reproductions with our compliments. Simply write to Dept. J-5.



**GREAT LAKES CARBON CORPORATION**

18 EAST 48TH STREET, NEW YORK 17, N.Y. OFFICES IN PRINCIPAL CITIES



## EDITORIAL STAFF

R. J. McKay, Chairman, Publication Committee  
Cecil V. King, Editor  
Norman Hackerman, Technical Editor  
Ruth G. Sterns, Managing Editor  
U. B. Thomas, News Editor  
H. W. Salzberg, Book Review Editor  
Natalie Michalski, Assistant Editor

## DIVISIONAL EDITORS

W. C. Vosburgh, Battery  
J. E. Draley, Corrosion, I  
R. T. Foley, Corrosion, II  
John J. Chapman, Electric Insulation  
Abner Brenner, Electrodeposition  
H. C. Froelich, Electronics  
D. H. Baird, Electronics—Semiconductors  
Sherlock Swann, Jr., Electro-Organic  
John M. Blocher, Jr., Electrothermics and Metallurgy, I  
A. U. Seybolt, Electrothermics and Metallurgy, II  
W. C. Gardiner, Industrial Electrolytic  
C. W. Tobias, Theoretical Electrochemistry, I  
A. J. de Bethune, Theoretical Electrochemistry, II

## REGIONAL EDITORS

Howard T. Francis, Chicago  
Joseph Schuelein, Pacific Northwest  
J. C. Schumacher, Los Angeles  
G. W. Heise, Cleveland  
G. H. Fetterley, Niagara Falls  
Oliver Osborn, Houston  
Earl A. Gulbransen, Pittsburgh  
A. C. Holm, Canada  
J. W. Cuthbertson, Great Britain  
T. L. Rama Char, India

## ADVERTISING OFFICE

ECS  
1860 Broadway, New York 23, N. Y.

## ECS OFFICERS

Norman Hackerman, President  
University of Texas, Austin, Texas  
Sherlock Swann, Jr., Vice-President  
University of Illinois, Urbana, Ill.  
W. C. Gardiner, Vice-President  
Olin Mathieson Chemical Corp., Niagara Falls, N. Y.  
R. A. Schaefer, Vice-President  
Cleveland Graphite Bronze Div., Clevite Corp., Cleveland, Ohio  
Lyle I. Gilbertson, Treasurer  
Air Reduction Co., Murray Hill, N. J.  
Henry B. Linford, Secretary  
Columbia University, New York, N. Y.  
Robert K. Shannon, Assistant Secretary  
National Headquarters, The ECS, 1860 Broadway, New York 23, N. Y.

# Journal of the Electrochemical Society

MAY 1958

VOL. 105 • NO. 5

## CONTENTS

### Editorial

Russian Literature ..... 90C

### Technical Papers

Indium as an Anode Material. T. L. Boswell..... 239  
Effect of Amines on Polarization of Iron Electrodes. A. F. Schram  
and L. R. Burns ..... 241  
Corrosion of Anodically and Cathodically Polarized Magnesium  
in Aqueous Media. G. R. Hoey and M. Cohen..... 245  
Investigations in the CuGaS<sub>2</sub>-ZnS and AgGaS<sub>2</sub>-ZnS Systems.  
E. F. Apple ..... 251  
The Effect of Impurities on the Plaque Brightness of a 3000°K  
Calcium Halophosphate Phosphor. A. Wachtel..... 256  
Polarographic Reduction of Delta-3-Ketosteroids in Well-Buffered  
Media. P. Kabasakalian and J. McGlotten..... 261  
Glow-Discharge Electrolysis in Aqueous Solutions. A. R. Denaro  
and A. Hickling ..... 265  
Vapor Pressure of Titanium Tetrabromide. E. H. Hall,  
J. M. Blocher, Jr., and I. E. Campbell..... 271  
Vapor Pressure of Titanium Tetrafluoride. E. H. Hall,  
J. M. Blocher, Jr., and I. E. Campbell ..... 275  
Mechanisms of Hydrogen Producing Reactions on Palladium,  
V. The Deuterium-Palladium System. S. Schuldiner and  
J. P. Hoare ..... 278  
Uncommon Valency Ions and the Difference Effect.  
M. E. Straumanis ..... 284

### Technical Note

A Technique for Purifying Electrolytic Solutions.  
D. A. Vermilyea ..... 286

### Current Affairs

Highlights of the January Board of Directors' Meeting..... 94C  
Section News ..... 95C Literature from Industry..... 99C  
Division News ..... 97C Announcements from  
Personals ..... 97C Publishers ..... 100C  
Letter to the Editor..... 97C Employment Situations ..... 101C  
News Items ..... 97C ECS Future Meeting Dates.. 288

Published monthly by The Electrochemical Society, Inc., from Manchester, N. H., Executive Offices, Editorial Office and Circulation Dept., and Advertising Office at 1860 Broadway, New York 23, N. Y., combining the JOURNAL and TRANSACTIONS OF THE ELECTROCHEMICAL SOCIETY. Statements and opinions given in articles and papers in the JOURNAL OF THE ELECTROCHEMICAL SOCIETY are those of the contributors, and The Electrochemical Society assumes no responsibility for them. Nondeductible subscription to members \$5.00; subscription to nonmembers \$18.00. Single copies \$1.25 to members, \$1.75 to nonmembers. Copyright 1958 by The Electrochemical Society, Inc. Entered as second-class matter at the Post Office at Manchester, N. H., under the act of August 24, 1912.

89C

กรมวิทยาศาสตร์  
กระทรวงมหาดไทย



## Russian Literature

**R**USSIAN scientific periodicals are not expensive to buy in the United States. We have listed what seem to be the most important chemical journals, ten in number, excluding biochemistry and abstract journals, and find that they can be obtained for \$162.00 per year, at present. Should our Libraries buy these journals, with the expectation that more and more readers will learn Russian? Or should a more comprehensive effort be made to put complete English translations on the library shelves? This is not a temporary problem, since Russian research will increase rather than decrease in importance. It is partly a question of economics: for example, can an industrial research organization better afford to support cooperative, competent translation services than possibly incompetent translation by its own staff? The probable rapid growth in volume of Russian literature must be considered.

The American Institute of Physics has found it possible to publish complete translations of the four leading Russian periodicals of Physics, selling yearly subscriptions at rates comparable to those for American journals. The translating and printing are done by Consultants Bureau, Inc. This project is subsidized by the National Science Foundation and the Atomic Energy Commission. Consultants Bureau, Inc., also translates five of the ten chemical journals mentioned above, and these are available at much higher rates.

A great many individual articles, book chapters, etc., have been translated and placed on sale in microfilm and photoprint form. The Translation Center at the John Crerar Library in Chicago acts as repository and clearinghouse for translations from all languages. It publishes a magazine, *Translation Monthly*, which lists all translations as received. (It solicits translations of Russian technical literature from companies and individuals, and will make them available to all.) This organization is subsidized by NSF, and charges only the usual page price for photocopy service. The Dept. of Scientific and Industrial Research, 5-11 Regent St., London, acts in a similar capacity and publishes a monthly list of new material.

If there were a Russian journal devoted mainly to Electrochemistry, we should urge the Society to sponsor full translation. Perhaps we can persuade someone to prepare a monthly list of titles of articles of interest, including details of translation availability, to be published in this JOURNAL.

Consultants Bureau, Inc., has announced a contract with the Soviet publication export agency for "exclusive" rights to publish translations in this country of twenty scientific periodicals, in return for royalty payments. Since the Russian and U. S. Governments have no copyright agreement, presumably no "exclusive" contract can be enforced; but active cooperation by the Soviet agency could confer a distinct competitive advantage.

In the long run, we may have to learn to read Russian, but we are making valiant efforts to avoid it. When will high-speed mechanical translators become available?

—CVK





... Greatly Reduced Clogging  
of Diaphragms

**NOW!**

... Lower  
Cell Maintenance Costs

... Longer Anode Life

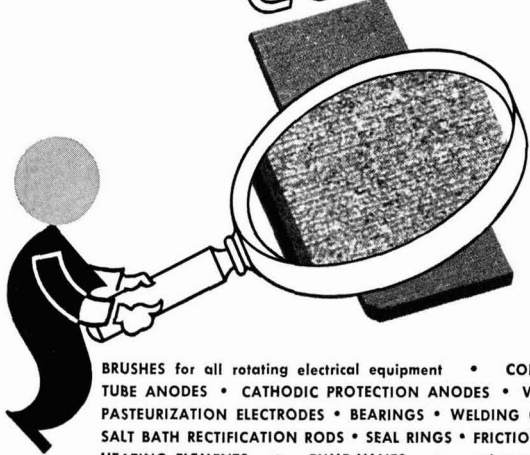
Costly, troublesome clogging of diaphragms due to the oil impregnant in conventional anodes, is materially lessened by the new Stackpole "GraphAnodes." Cell maintenance costs are reduced accordingly.

Better results are achieved because Stackpole *GraphAnodes* present a uniform, low-porosity surface to the electrolyte. The graphite is consumed slowly and evenly. It does not slough off to clog the diaphragm or contaminate the cell.

Let Stackpole arrange for a convincing demonstration of these new anodes on your own equipment. You be the judge—and, by way of convincing proof we suggest that you pay particular attention to the reduced frequency of diaphragm renewals.

**STACKPOLE CARBON COMPANY**  
St. Marys, Pa.

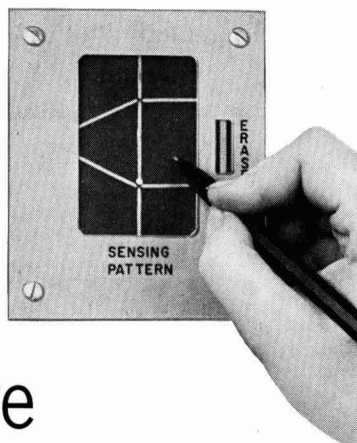
# STACKPOLE GraphAnodes



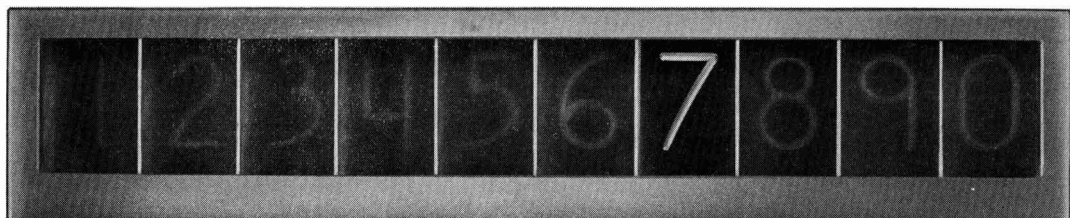
MAGNIFIED, UNRETOUCHED PHOTO ... shows uniform structure of Stackpole *GraphAnodes*. The low-porosity surface assures that electrolyte will act on the surface, not below to cause premature anode deterioration and cell contamination by droppings of unconsumed graphite particles.

BRUSHES for all rotating electrical equipment • CONTACTS (carbon-graphite and metal powder types)  
TUBE ANODES • CATHODIC PROTECTION ANODES • VOLTAGE REGULATOR DISCS • WATER HEATER and  
PASTEURIZATION ELECTRODES • BEARINGS • WELDING CARBONS • MOLDS AND DIES • POROUS CARBON  
SALT BATH RECTIFICATION RODS • SEAL RINGS • FRICTION SEGMENTS • CLUTCH RINGS • ELECTRIC FURNACE  
HEATING ELEMENTS • PUMP VANES • and many other carbon, graphite, and electronic components.

# Write a numeral here



# and read it here

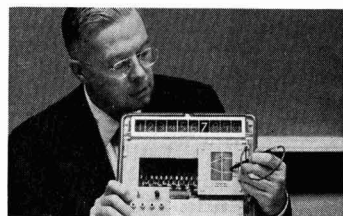


# on new Bell Labs machine

A new device invented at Bell Laboratories "reads" a numeral while it is being written and instantly converts it into distinctive electric signals. The signals may be employed to make a numeral light up in a display panel, as above, or they may be sent to a computer or to a magnetic "memory" for storage.

The writing is done with a metal stylus on a specially prepared surface. Two dots, one above the other, are used as reference points. Seven sensitized lines extend radially from the dots. Transistorized logic circuits recognize numerals according to which lines are crossed.

The concept of a number-reader has interesting possibilities as a new means of communication from humans to machines. For example, in an adjunct to a telephone, it might provide inexpensive means of converting handwritten data into signals which machines can read. The signals could be transmitted through the regular telephone network to a teletypewriter or computer at a distant point. In this way, a salesman might quickly and easily furnish sales data to headquarters, or a merchant might order goods from a warehouse.



Modern communication involves many more fields of inquiry than the transmission and reception of sound. The experimental number-reader is but one example of Bell Telephone Laboratories work to improve communications service.

Tom Dimond, a B.S. in E.E. from the University of Iowa, demonstrates an experimental model of his number-reading invention. A similar device can also be made to read alphabetical characters. Small size and low power requirements result from transistor circuitry.



**BELL TELEPHONE LABORATORIES**

World Center of Communications Research and Development



# Indium as an Anode Material

T. L. Boswell

*Research and Development Division, Elgin National Watch Company, Elgin, Illinois*

## ABSTRACT

Indium and its alloys with bismuth and lead are evaluated as energy producing electrodes for use in small sealed cells. The value of bismuth as an alloying element in promoting the ability of the electrode to function at high current densities is discussed and the electrical capacity, voltage stability, and temperature voltage coefficient of alkaline cells with mercuric oxide cathodes are given.

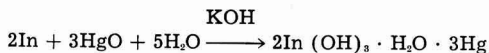
Indium possesses a high hydrogen overvoltage (1), near that of Hg and its standard potential is close to that of Cd. These two properties indicated that it might be useful as an energy producing anode and might show less tendency toward parasitic reactions which promote deterioration of commercial cells during storage.

For instrument applications where weight and volume are at a premium it was desirable to know how In would compare with other commonly used metals. On a per Faraday basis: Zn, 32.69 g, 4.57 cc; In, 38.27 g, 5.24 cc; Cd, 55.48 g, 6.42 cc; thus In is within the range of weight and volume for useful commercial anodes.

Data on the alkali resistance of indium-containing solders (2) indicated that In alloys could remain in contact with alkaline electrolytes without an appreciable reaction rate. While that work was performed on alloys of low In content (50% or less), it was not unreasonable to expect the same or lower rates of attack on alloys richer in In. Some work in this laboratory, although not yet complete, indicates that In base alloys are much more resistant to attack by alkali electrolytes than more commonly used metals, even when these other metals are protected with inhibitors.

Little consideration has been given to the use of In as an anode prior to the present work (3). Latimer (4) estimated the standard potential to be 1.18 v for the reaction in which the oxide is formed and 1.0 v for the reaction in which the hydroxide is formed (5).

For purposes of this experimental work the following equation has been assumed to be correct:



While the exact composition of the In compound formed is not known precisely, there is analytical evidence that it approaches the composition given above and that, within the experimental error, the quantity of electricity obtained agrees with the combining ratios represented in the above equation.

## Experimental Results

It was recognized that one of the most serious problems to overcome was indium's lack of hard-

ness and strength. Its tendency to flow under low stresses made it difficult to maintain tight connections at the anode terminal. An examination of the available equilibrium diagrams in the literature showed that a number of binary systems existed containing single phase areas rich in In and that an appreciable increase in hardness could be obtained by using these alloys. Several of these alloys have been studied as anodes with some gratifying results. Jaffe and Weiss (6) had reported that the strongest alloys could be obtained with Pb, but that Bi was the most potent hardening element when added to In in small quantities. As it was desirable to keep In content as high as possible, consistent with the strength requirements, the Pb and Bi alloys were studied concurrently.

The binary In-Pb alloys were complete failures as anodes due to polarization at low current densities. It is quite possible that this effect is caused by the formation of PbO<sub>2</sub> on the electrode surface during cell action. This might subsequently be reduced to spongy Pb by local action, because when such an electrode is polarized and then permitted to recover there is a voltage plateau which corresponds to the lead potential.

Quite the opposite effect is found for the In-Bi alloy anodes. Pure In serves well as an anode at low to moderate current densities, but polarizes at higher current densities, making it undesirable for high-current applications. When Bi is added to In the resulting alloy has the ability to maintain its voltage at considerably higher current densities. An additional advantage is gained from use of the In-Bi alloy anodes in that many metals which poison In are present in the commercial grades and their deleterious effect can be neutralized by intentionally adding Bi in sufficient quantities.

The ternary alloys containing Bi have not yet been properly evaluated, but preliminary experiments indicate that they will be useful as anodic materials. They are stronger than either pure In or the binary alloys, thus overcoming one of the most serious limitations to the use of In anodes.

In order to evaluate the performance of In and In alloy anodes, a series of experiments was made with small sealed cells using HgO cathodes and

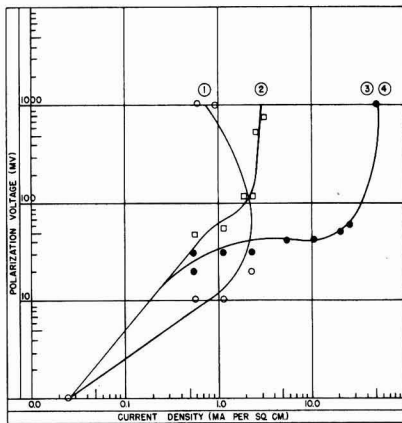


Fig. 1. Polarization of In and In alloy anodes. Each value represents the average of 5 cells. 1, commercial In; 2, 2.5% Pb-In; 3, 5% Bi-In; 4, 1.5% Pb, 2.5% Bi-In.

containing a third electrode of the anode material. By measuring the voltage between this reference electrode and the working anode or cathode, one can differentiate between anodic and cathodic polarization effects.

Successive loads were placed across the cells and voltage measurements were taken after the current had been flowing for 15 min for each load. The voltage between the reference and working anode is then a measure of the decrease in potential of the working anode due to the current flow. These data are plotted in Fig. 1.

At low current densities (2.3 ma/cm<sup>2</sup>) pure In shows lower polarization characteristics than any of the alloys but quickly polarizes to an unusable extent if higher current densities are attempted.

When Pb is added to In these polarization effects are increased and the electrode ceases to be useful even at the lower current densities.

When Bi is present either in binary alloys or in

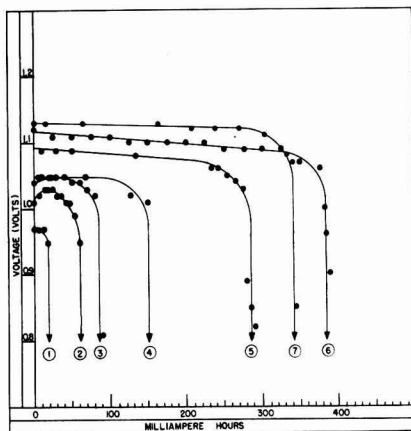


Fig. 2. Discharge curves for 5% Bi-In-HgO cells with an alkaline electrolyte. Theoretical capacity of these cells is 400 ma/hr. Each value represents the average on 5 cells. 1, 80 ma; 2, 60 ma; 3, 40 ma; 4, 20 ma; 5, 10 ma; 6, 5 ma; 7, 2 ma.

the ternary alloy with lead, the electrode can function at much higher current densities, remaining useful up to about 31 ma/cm<sup>2</sup>.

For evaluation tests a small sealed cell was designed using a HgO cathode and an alkaline electrolyte. This cell was 5/8 in. square x 2/10 in. thick. The electrodes were arranged facing one another and attached to the square faces of the cell. Such cells had a 400 ma-hr theoretical capacity and an apparent electrode area of 1.88 cm<sup>2</sup>.

Figure 2 shows the discharge curves for a group of these evaluation cells at various current densities. The end points were taken at first polarization under continuous drain. An appreciable fraction of this theoretical service is obtained at current densities up to 5.3 ma/cm<sup>2</sup>. If the cells were permitted to recover, further capacity could be obtained, especially from those cells discharged at the higher currents. The constancy of their voltage during discharge is quite noteworthy. At intermediate to high current densities a slight rise in voltage is noted during discharge. At present an adequate explanation for this characteristic cannot be given. The cell potential also rises during storage under open circuit conditions.

To determine the variation of potential with storage time, groups of the evaluation cells were stored at room temperature, some under open circuit conditions and some with small currents being drawn continuously. Voltage measurements were made with an L&N type K-2 potentiometer. At first, readings were taken each day, then on three days each week, and finally on two days each week. The results of these tests over an 18 month period are shown in Fig. 3.

The tendency of In cells to maintain their voltage is well illustrated by these data. These first results indicate that the In electrode has an excellent inherent possibility as a secondary voltage standard. While no study has been made to achieve the optimum design, it was noted that small voltage fluctuations were superimposed on the curves shown in the figure which could be correlated to room temperature changes. Of particular interest is the fact that reversal of the direction of voltage fluctuation with temperature changes occurred between unloaded cells and those where current was flowing. This suggests a possible means of compen-

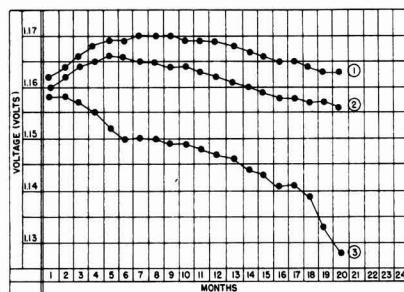


Fig. 3. Voltage stability at continuous loads indicated. Each value represents the average of at least 8 readings on 5 cells. 1, no current; 2, 1  $\mu$ a; 3, 10  $\mu$ a.



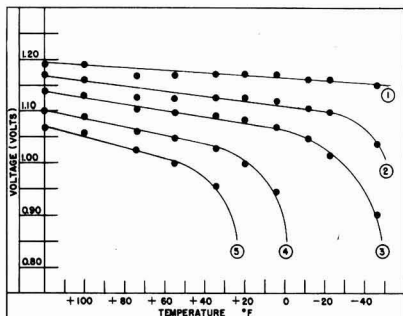


Fig. 4. Voltage-temperature-current density relationship of 5% Bi-In-HgO alkaline cells. Each value represents the average of 10 cells. 1, 0.003 ma/cm<sup>2</sup>; 2, 0.12 ma/cm<sup>2</sup>; 3, 0.68 ma/cm<sup>2</sup>; 4, 3.29 ma/cm<sup>2</sup>; 5, 6.36 ma/cm<sup>2</sup>. Current densities were calculated at 23.3°C.

sating for room temperature changes when using this type of cell as a voltage reference.

Another important aspect of a cell containing this electrode is its operation at various temperatures. Figure 4 shows the voltage-temperature relationship at various current densities for a group of the same evaluation cells.

These data represent the average results obtained on 10 cells. The cells were placed in a temperature chamber and permitted to come to temperature. Voltage readings were then taken after the current had been flowing for 15 min. Some values were taken after the cells had been at temperature for just 3 hr and then rechecked after 24 hr. Ex-

cellent agreement between the two sets of readings was obtained.

From the linear relationship shown in Fig. 4, the temperature coefficient of voltage varied between 0.00080 to 0.00232 v/°C (0.00044 to 0.0013 v/°F) between 12.8 and 37.8°C (+55 and +100°F) with the larger coefficient associated with the larger current density as expected.

### Conclusion

These preliminary results indicate that In can be stored in alkaline electrolytes without deterioration and yet function usefully at the proper time. It is believed that these characteristics make further studies desirable.

Manuscript received Sept. 23, 1957. This paper was prepared 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 1958 JOURNAL.

### REFERENCES

1. T. Moeller and B. S. Hopkins, *J. (and Trans.) Electrochem. Soc.*, **93**, 84 (1948).
2. S. M. Grymko and R. I. Jaffe, *Materials & Methods*, **31**, 59-60, March (1950).
3. T. L. Boswell, U. S. Pat. 2,683,184, July 6, 1954.
4. W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," pp. 149-151, Prentice-Hall Inc., New York (1938).
5. W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," pp. 161, Prentice-Hall Inc., New York (1952).
6. R. I. Jaffe and S. M. Weiss, *Materials & Methods*, **36**, 113-15, September (1952).

## Effect of Amines on Polarization of Iron Electrodes

Alfred F. Schram, and Lawrence Raymond Burns<sup>1</sup>

*Chemistry Department, Agricultural and Mechanical College of Texas, College Station, Texas*

### ABSTRACT

An apparatus has been designed and constructed which gives a measure of the effect of organic amine salts on the polarization of iron cathodes in 1.0N sulfuric acid solution. The apparatus consists essentially of a Wheatstone Bridge circuit in which two of the ratio arms are electrolysis cells with a common anode and separate iron cathodes. The elements of the bridge are arranged in such a way that the electrolysis currents through the two cathodes can be measured simultaneously when the cathodes are at the same potential.

The effect of the amine salts on the polarization of the iron cathodes has been interpreted in terms of the apparent area changes brought about by adsorption of the amines on the surface of the cathodes. These apparent area changes have then been compared with the per cent inhibitor efficiencies of the amines, as measured by corrosion rate studies. Over the concentration ranges employed, the per cent inhibitor efficiency for each amine is a linear function of the apparent per cent surface area masked by that amine. Since the different amines showed considerable specificity in the relationship between per cent efficiency and apparent per cent area masked, it is concluded that the action of the amine as a corrosion inhibitor is more than a simple masking of certain portions of the surface of the corroding metal.

In the past few years considerable attention has been given to the effect of various substances, both organic and inorganic, on polarized electrodes and

on corroding metals. Many organic colloids such as agar, egg albumen, and gum tragacanth, are known to retard the action of acids or pure water upon zinc or iron. The salts of arsenic, antimony,

<sup>1</sup> Present address: The Texas Company, Port Arthur, Texas.

and mercury, as well as many organic nitrogen and sulfur compounds, inhibit the attack of acids on metals. Different explanations have been proposed for the mechanism of these phenomena.

Some investigators have shown that organic amines in general affect the cathodic polarization of various metals, and have little or no effect on the anodic polarization (1, 4). They assert that these materials increase the hydrogen overvoltage at the cathodic areas and thus hinder the discharge of hydrogen ions. Others hold that the inhibitors are adsorbed over the entire surface, but are held more strongly at the anode areas where, by increasing the effective electron density, they prevent the dissolution of the metal from these areas (5).

A detailed theory of the mechanism of the inhibiting action of nitrogen-containing organic compounds was proposed by Mann (6) as a result of investigations carried out by himself and co-workers on the acid corrosion of steel.

Mann and Shih-Jen Ch'iao (4) investigated the possibility of a quantitative relationship between the rise in cathode potentials of polarized electrodes and the decrease in corrosion rates as determined by actual corrosion rate studies.

Mann and his co-workers investigated fourteen different amines by this method. They found that the two methods could be correlated quantitatively, and that the potential rise method was satisfactory as a means of estimating the effectiveness of the amines as corrosion inhibitors.

The purpose of the present investigation was to design and construct an apparatus which could test the theory proposed by Mann (6) that the effect of amine inhibitor ions on the surface of the corroding metal could be explained in terms of the fraction of metal surface effectively shielded by the inhibitor.

The amines used in the present work were compounds that differed from one another in structural configuration or in molecular weight. Two aliphatic amines, di-*n*-propylamine and di-*n*-butylamine; one aromatic amine, dimethylaniline; and one substituted aliphatic amine, beta-bromoethylamine, were investigated.

## Apparatus

### The Dual Cathode Bridge

The apparatus employed (Fig. 1) was essentially a Wheatstone bridge circuit in which the two lower arms of the bridge were branches of a three-compartmented electrolysis vessel, each compartment being separated from the others by fritted disks. A platinum anode in the center compartment of the vessel was contained within a glass sleeve. A hole approximately 1 cm<sup>2</sup> in area in the wall of the sleeve enabled current to flow from the anode to the two cathodes mounted in the two end compartments of the vessel. By rotating the glass sleeve it was possible to vary the effective path lengths between the common anode and the two cathodes, and thus, by compensating for any difference in porosity between the two fritted disks,

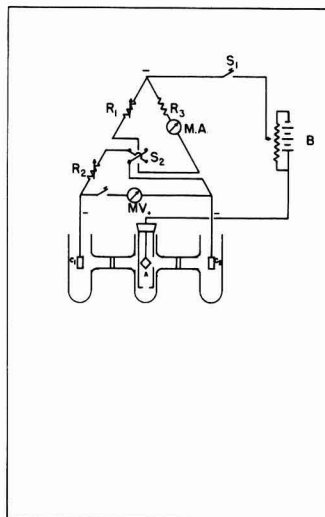


Fig. 1. Dual cathode bridge.  $S_1$ , Knife blade switch; B, 6 v d-c source;  $R_1$ ,  $100 \pm 0.1 \Omega$  helipot;  $R_2$ ,  $100 \pm 0.1 \Omega$  helipot;  $R_3$ ,  $15 \Omega$  fixed resistor; M.A., milliammeter; M.V., millivoltmeter;  $C_1$ , left cathode;  $C_2$ , right cathode; A, anode.

to maintain the same solution resistance in both branches of the cell.

The electrolytic paths through each branch of the cell constituted the two lower resistance arms of the bridge circuit. The two upper resistance arms consisted of the following: a pair of 100-ohm precision variable resistances in series formed one of the arms; and a milliammeter connected in series with a 15-ohm fixed resistance formed the other arm. A millivoltmeter was connected across the two cathodes and served as the null indicator for the bridge.

A double-pole-double-throw switch was connected in the upper part of the bridge circuit in such manner that when the total resistance of the arm containing the milliammeter was carefully matched by means of one of the variable resistances in the opposing arm of the bridge, the milliammeter could be connected alternately in series with either cathode without upsetting the balance of the bridge. This enabled one to read the current flowing in either branch of the electrolysis vessel with the bridge at balance.

The two cathodes were cut from the same piece of metal stock and machined to the same shape and size, with a tolerance of less than 0.001 in. being allowed in any linear dimension. A projection of the cathode metal left on one side of each cathode allowed them to be sealed into Pyrex glass tubes by means of Dekotinsky cement. The metal projection extending through the cement was soldered to a strip of copper wire. The back and sides of each cathode were masked off with a Tygon base primer and then coated with paraffin. The electrodes were mounted in the two end compartments of the electrolysis vessel in such a way that the unmasked face of each cathode was parallel with, and directed toward, the common anode contained in



the center compartment. Special V-slotted electrode holders make it possible to remove the electrodes from the vessel and to replace them again in nearly identically the same positions. Immediately before each run, the cathodes were freshly sanded with 6/0 garnet paper, rinsed with conductivity water, and dried with filter paper.

*Operation of the bridge.*—In operation,  $R_1$  (Fig. 1) was first adjusted so that its resistance was equal to the sum of  $R_2$  plus the internal resistance of the milliammeter. This was accomplished by setting  $R_2$  to zero and replacing the two branches of the electrolysis cell with a pair of L&N standard wire-wound resistances, each having a resistance of 10 ohms. Switch  $S_1$  was then closed and  $R_1$  was adjusted until the millivoltmeter was at null. At this point the resistance of  $R_1$  was equal to the total resistance of the milliammeter-containing arm of the bridge, and the switch  $S_2$  could be reversed without changing the balance of the bridge.

One normal sulfuric acid was placed in all three compartments of the cell, and the prepared iron cathodes and the platinum anode were connected in the circuit and placed in their respective compartments. Electrolysis was carried on until the cathodes reached equilibrium. The glass sleeve surrounding the anode was rotated until, with the bridge balanced, the current was the same in the two branches of the cell. At this point, the resistance across the left branch of the cell was equal to the resistance across the right branch, and the

apparatus was ready for use. Once set in this fashion, it was found that the cathodes could be interchanged in the two end compartments with a resulting change of less than 1/10 ma in the difference between the two values of current flowing in the two branches of the cell.

With the bridge balanced as described above, the effect of amine inhibitors on the polarized iron cathode was studied by replacing the solution in the left compartment of the vessel with inhibited acid, waiting until a steady state was reached, and then rebalancing the bridge by adjusting  $R_2$  until the millivoltmeter indicated that left and right cathodes were at the same potential. Current readings were then taken in the two branches of the cell at a number of different current levels. Data were obtained in this manner for various concentrations of the four different amines investigated. For each amine, at each concentration, the per cent decrease caused by the presence of the inhibitor in the left branch of the cell proved to be independent of the current level at which the bridge was operated. This fact is shown graphically in Fig. 2-5, in which the decrease in current in each case is plotted against the current in the uninhibited branch of the cell. The plots are straight lines, the slopes of which represent the percentage decrease in current caused by the presence of the inhibitor.

*Use of the dual cathode bridge.*—To determine the response of the bridge to known changes in the area of exposed surface of one cathode, the area of

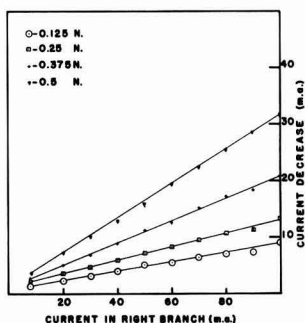


Fig. 2. Response of the dual cathode bridge to di-n-butylamine.

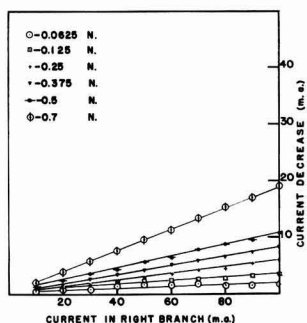


Fig. 4. Response of the dual cathode bridge to dimethylaniline.

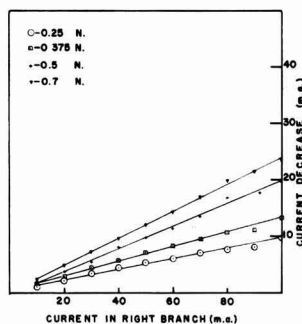


Fig. 3. Response of the dual cathode bridge to di-n-propylamine.

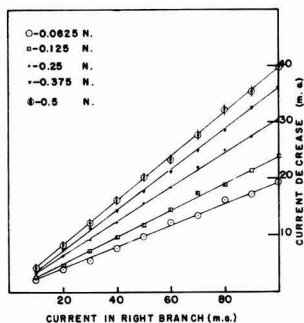


Fig. 5. Response of the dual cathode bridge to  $\beta$ -bromoethylamine.

exposed surface of the other cathode being held constant, the following experiment was performed.

Uninhibited 1N H<sub>2</sub>SO<sub>4</sub> was placed in all compartments of the electrolysis vessel, and the bridge was balanced in the manner previously described. One of the cathodes was then removed, washed, sanded, dried, and one-third of the exposed surface was coated carefully with paraffin. The electrode was replaced in the cell and current readings in the two branches were taken at different current levels. This procedure was repeated with different fractions of the area of the electrode face being masked with paraffin. It was found that the percentage decrease in current in the left branch was independent of the current level used, and depended only on the fraction of electrode face masked by the paraffin. A graph of per cent of cathode face masked vs. per cent current decrease in the left branch was prepared (Fig. 6) and was used in the later experiments with the amine inhibitors to derive a value for the per cent decrease in surface area caused by adsorption of the amine onto the surface of the cathode. Because of the many factors involved, this value as read from Fig. 6 may not represent the true percentage decrease in surface area in the case of the shielding of the surface by the adsorbed amine. But because the percentage decrease in electrolysis current upon shielding one cathode—either by paraffin coating or by adsorbed amine—was always independent of the current level at which the bridge was operated, the values obtained from Fig. 6 must be related in some simple fashion to the true area decrease in each case. Thus the values read from Fig. 6 may be taken as at least an indirect measure of the relative amount of shielding of the electrode surface by the adsorbed amine. In this sense, the effect of each amine could be interpreted in terms of the relative or apparent area changes at the electrodes. The effectiveness of the amines in shielding the surface could then be compared in a relative fashion to their effectiveness in inhibiting corrosion, the latter being measured by the corrosion rate method.

In studying the effect of the amine inhibitors on the polarized iron electrode, the cathodes were

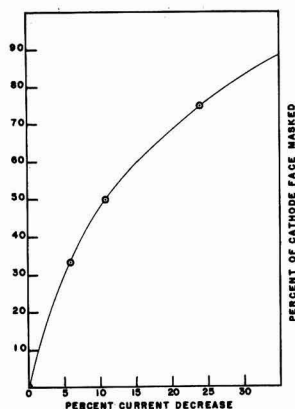


Fig. 6. Per cent current decrease vs. per cent of cathode face masked.

freshly sanded before each run, rinsed with conductivity water, dried, and all but one face of each were freshly coated as previously described. Inhibited acid solution was put into the left compartment, and uninhibited acid solution into the other two compartments. All solutions had been previously subjected to electrolysis with platinum electrodes in order to remove traces of metallic impurities, and all water used in preparation had been previously distilled from alkaline permanganate and stored in Pyrex bottles.

The electrodes were placed in the electrolysis vessel, and electrolysis was carried out until the electrodes reached equilibrium or a steady state. The bridge was balanced, and readings of current taken in both branches of the cell. In all cases it was found that the percentage decrease in current caused by the presence of the inhibitor was essentially independent of the current level at which the bridge was operated.

### Discussion

In determining the per cent inhibitor efficiencies of the four amines used in the polarization studies, mild steel coupons were cut from the same metal stock as the cathodes, and were used in measuring the inhibitor efficiencies of the amines. The per cent inhibitor efficiencies are shown in Table I.

Table I shows the value of the per cent electrode area masked, as read from Fig. 7, compared with the corresponding per cent inhibitor efficiencies as determined by the corrosion rate method. The same data are shown graphically in Fig. 7. Both the table and the graph show that the per cent inhibitor efficiency for a given amine seems to be a linear function of the amount of masking of the metal surface by the adsorbed amine ion. However, it is not directly proportional to the amount of masking,

Table I. Comparison of apparent cathode area masked with inhibitor efficiency of amine salts

Inhibitor	Normality (of amine salt)	% Current decrease	% Apparent cathode area masked (from Fig. 6)	% Inhibitor efficiency (by corrosion rate method)
Di- <i>n</i> -propylamine	0.25	10	47	75.3
	0.375	14	59	78.0
	0.5	20	70	80.0
	0.7	24	75	—
Dimethylaniline	0.0625	3	17	60.5
	0.125	4.5	25	62.3
	0.25	6	33	67.0
	0.375	8.5	42.5	71.5
	0.5	11	50	73.0
	0.7	19	68	—
Di- <i>n</i> -butylamine	0.125	9	44	78.4
	0.25	14	58	79.1
	0.375	22	73	81
	0.5	33	82	82.2
Beta-bromoethylamine	0.0625	20	70	83.2
	0.125	24.5	75.5	84.5
	0.25	33.15	81	89.2
	0.375	35.5	84	90.8

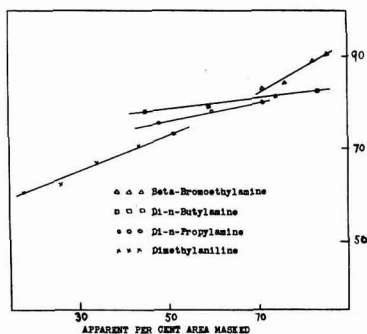


Fig. 7. Apparent per cent cathode area masked vs. inhibitor efficiency of amine salt.

and hence it is to be concluded that the action of amine salts in inhibiting corrosion is more complex than a simple percentage-wise blocking off of portions of the metal surface. The fact that consider-

able specificity is shown by the individual amines helps to confirm further that conclusion.

Manuscript received July 8, 1957. This paper is based on a thesis presented to the faculty of the Graduate School, A. and M. College of Texas by L. R. Burns in partial fulfillment of the requirements for the M.Sc. degree.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1958 JOURNAL.

#### REFERENCES

1. E. L. Chappell, B. E. Roetheli, and B. Y. McCarthy, *Ind. Eng. Chem.*, **20**, 582 (1928).
2. J. C. Warner, *Trans. Electrochem. Soc.*, **55**, 287 (1929).
3. F. H. Rhodes and W. E. Kuhn, *Ind. Eng. Chem.*, **21**, 1066 (1929).
4. C. A. Mann and Shih-Jen Ch'iao, *ibid.*, **39**, 910 (1947).
5. N. Hackerman and A. C. Makrides, *ibid.*, **46**, 523 (1954).
6. C. A. Mann, B. E. Lauer, and C. T. Hultin, *ibid.*, **28**, 159 (1936).

## Corrosion of Anodically and Cathodically Polarized Magnesium in Aqueous Media

G. R. Hoey and M. Cohen

Division of Applied Chemistry, National Research Council, Ottawa, Ontario, Canada

#### ABSTRACT

The effect of current density, pH, and temperature on the anodic behavior, cathodic behavior, and corrosion of magnesium in aqueous solutions has been studied. A tentative mechanism for the anodic oxidation of magnesium is postulated. Local corrosion and/or undermining of metallic magnesium at the anode are appreciable and may, in fact, account for the observed low anodic current efficiencies of magnesium. An intergranular type of corrosion occurs at cathodically polarized magnesium at elevated temperatures. A hydrogen embrittlement theory is proposed to explain intergranular cathodic corrosion.

The magnesium electrode,  $Mg; Mg^{++}$ , behaves as an irreversible electrode in aqueous solutions. The potential of Mg is considerably more noble than the electrochemical potential calculated from thermodynamic data and is practically independent of the magnesium ion concentration (1, 2). The possible causes of the wide departure from reversibility are: (a) the electrochemical process involves magnesium ions with abnormal valencies; (b) self-corrosion; (c) film formation; and (d) activation and concentration overpotential. The last of these four possibilities is relatively unimportant for Mg. To determine the importance of the various processes the electrode is studied under nonreversible operating conditions, that is, under experimental conditions of anodic and cathodic polarization.

The anodic dissolution of Mg has been studied extensively (3-8). The outstanding experimental facts of the dissolution which, as yet, are not satisfactorily explained are: (a) the anodic current efficiency in aqueous solutions is less than 100% (the anodic current efficiency is defined as the ratio of

the actual coulombs passed to the theoretical coulombs obtainable from the actual weight loss assuming a magnesium valency of two); (b) the amount of hydrogen produced in the absence of added oxidizing agents is equivalent to the excess Mg dissolved at the anode; and (c) the corrosion film formed on Mg is composed of Mg, MgO, and  $Mg(OH)_2$  (9-13).

The electrochemical formation of monovalent Mg (3, 4, 5, 8, 14) has been postulated by various workers to account for the low current efficiencies; solution reactions of  $Mg^+$  were postulated to account for the hydrogen and corrosion product formation. Robinson (6) has suggested that the low current efficiencies may be due to an enhanced corrosion rate at the anode since in an unbuffered solution the acidity at the metal-solution interface is higher than in the bulk of the solution for anodically polarized Mg.

Müller has studied the anodic passivity of Mg in  $H_2SO_4$ ,  $HNO_3$ ,  $NaOH$ , and  $MgCl_2$  solutions (15). In  $H_2SO_4$  solutions the current-time curves were simi-

lar to those obtained with other metals. Magnesium becomes passive in  $\text{HNO}_3$  solutions, but side reactions complicate the phenomenon. Passivity is not reached in  $\text{MgCl}_2$  solutions. Passivity in  $\text{NaOH}$  solutions results quickly, beyond which stage the current rises slowly. At cell potentials  $>6$  v only low current values are attained, whereas, at cell potentials  $<6$  v, values of almost half of the initial current are attained. The anodic polarization curves of Mg are flat at current densities up to  $1 \text{ ma cm}^{-2}$  in solutions containing ions which form soluble Mg salts; in the presence of ions such as  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{BO}_3^-$ , and  $\text{PO}_4^{3-}$  the anode polarizes (6).

Evans, *et al.*, (16) and Phelps (17) have measured the cathodic polarization curves of Mg at room temperature. These authors observed a break in the potential-current curve similar to the cathodic polarization curves for iron. Phelps correlated the value of the current at this break with the corrosion current for a rotating Mg cathode.

The open circuit potential of Mg is practically constant in the pH range 3-11 and the corrosion rate increases slightly in this pH range in unbuffered solutions (18). At pH's  $>11$ , the potential curve shows a sharp bend toward more noble potentials and the corrosion rate shows a corresponding decrease. In buffered solutions (19) the sharp increase in potential occurs at  $\text{pH} = 9.2$ . A marked increase in potential and corrosion rate also occurs at pH's  $<3$ . The acid dissolution of Mg is probably diffusion controlled (20-24). Casey and Bergeron (25) interpreted the acid dissolution of Mg in terms of the physical control of diffusion by surface films of  $\text{Mg}(\text{OH})_2$  and/or by oxide.

The effect of temperature on the electrochemical behavior of Mg has received comparatively little attention. The current efficiency of Mg in 3% NaCl solution assuming a Mg valency of two is approximately 50% and is independent of temperature in the range  $0^\circ\text{-}50^\circ\text{C}$  (8). The activation energy for dissolution of Mg in acids varies from 3-5 kcal mole $^{-1}$  (20, 23). Electron diffraction data indicate a hexagonal  $\text{Mg}(\text{OH})_2$  is formed at room temperature, whereas a film of  $\text{Mg}(\text{OH})_2$ , presumably rhombic, is formed at  $100^\circ\text{C}$  which is more protective than the film formed at room temperature (12).

In this paper a study of the effect of temperature, pH, and current density on the anodic, cathodic, and open circuit behavior of Mg is presented.

### Experimental

Commercially pure distilled Mg obtained from Dominion Magnesium Ltd. was used. This material is reported to have a minimum purity of 99.96% with a total Fe, Ni, and Cu content not greater than 0.005%. Solutions were prepared from reagent grade salts. Experiments were performed using unbuffered and buffered solutions of 110 ppm NaCl. Sodium hydroxide-sodium borate, boric acid-sodium borate, and sodium carbonate-sodium bicarbonate buffers were used for pH's up to 10. Sodium hydroxide was used to obtain pH's  $>10$ . The pH's of the NaOH solutions were calculated using values of the dissociation constant of water  $k_w = 1.0 \times 10^{-14}$  at  $25^\circ\text{C}$  and  $k_w = 1.9 \times 10^{-13}$  at  $75^\circ\text{C}$  (26). The pH's

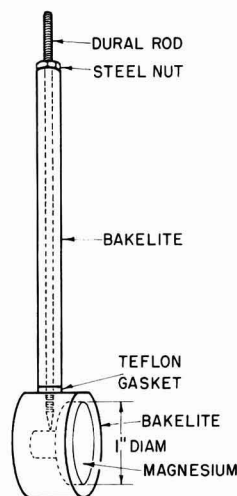


Fig. 1. Magnesium electrode

of the buffered solutions at  $75^\circ\text{C}$  were determined using a calibrated Ag; AgCl-glass electrode assembly and a Beckman pH meter. Standard buffer solutions were used for the calibration of the electrode assembly (27).

The electrolytic cell consisted of a Mg cathode and a Mg anode with a Ag;AgCl probe reference electrode (thermal electrolytic type) at both Mg electrodes immersed in aqueous solution. Potentials of the Ag;AgCl half-cell were calculated using the data of Bates and Bower (28). The Mg electrode used for most experiments is illustrated in Fig. 1. The Mg specimen was annealed at  $300^\circ\text{C}$  for 2 hr in an argon atmosphere, polished on 1/0 emery paper, degreased, etched in 0.1N HCl for 1 min, weighed, and moulded in bakelite. The bakelite button was then machined and the electrode assembled. In basic solutions ( $>0.01\text{N}$  NaOH) Mg rods ( $\frac{1}{4}$  in. diameter x 7 in. long) were used as electrodes since the bakelite decomposed in these solutions at the higher temperatures.

A constant temperature oil-bath regulated to within  $1^\circ\text{C}$  was used. Fresh solution was continuously supplied to the cell solution ( $\frac{1}{2}$  l) at the rate of  $\frac{1}{4}$  l/hr using an overflow system. The cells were maintained at constant current by discharging a d-c voltage supply (112.5 v) through an appropriate variable resistance, a calibrated ammeter, and the cell. Potentials were recorded on a L&N Speedomax recorder. Experiments were from 5 to 7 days duration.

The Mg specimen could be cracked from the bakelite by pressing it between the jaws of a vice. Corrosion products were removed from the Mg in boiling 15% chromic acid containing 1% silver chromate and the weight loss of the Mg determined.

The corrosion products of the Mg were analyzed by x-ray analysis. The corroded Mg specimens were examined metallographically.

### Results

The current efficiencies (%) of Mg anodes, the corrosion rate (m.d.d.) at the cathodes, the anodic

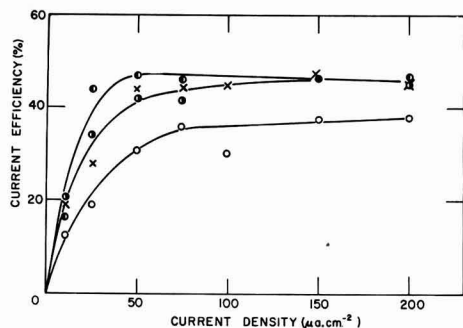


Fig. 2. Dependence of the current efficiency (%) of Mg anodes in 110 ppm NaCl solution on the current density: pH = 10 to 9; open circle, ca. 25°C; circle, right half solid, 58°C; circle, left half solid, 75°C; X, 92°C.

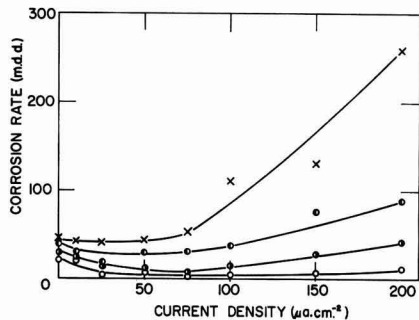


Fig. 3. Dependence of the corrosion rate of magnesium cathodes in 110 ppm NaCl solution on the current density: pH = 10 to 9; open circle, ca. 25°C; circle, right half solid, 58°C; circle, left half solid, 75°C; X, 92°C.

and cathodic polarization curves of Mg (steady potentials attained after several days immersion) in 110 ppm NaCl solutions are plotted vs. the current density ( $\mu\text{a cm}^{-2}$ ) for the temperatures 25°, 58°, 75°, and 92°C in Fig. 2, 3, and 4, respectively. It was found that the current efficiency of the Mg anode and the corrosion rate at the Mg cathode at a current density of 500  $\mu\text{a cm}^{-2}$  at 75°C in 110 ppm NaCl solutions is independent of time in the range 2-10 days.

The effect of pH on the current efficiency of Mg at a current density of 500  $\mu\text{a cm}^{-2}$  and the temperatures 25°C and 75°C is shown in Fig. 5. Log [Corrosion Rate (m.d.d.)] of Mg cathodes polarized at 500  $\mu\text{a cm}^{-2}$  and unpolarized Mg is plotted vs. the pH for the temperature 25°C in Fig. 6 and for the temperature 75°C in Fig. 7. Photographs demonstrating the various types of attack of the Mg which was observed are shown in Figs. 8, 9, 10 and 11.

Magnesium hydroxide was identified by x-ray diffraction analysis on the cathodes, anodes, and locally corroding specimens of Mg in 110 ppm NaCl solutions at the various temperatures studied. Free Mg metal particles were observed by the microscope in the corrosion products.

Cathodic polarization of Mg does not affect the lattice parameters of Mg. The values of a nonetched Mg specimen annealed in vacuum at 350°C are  $a_0 = 3.203$  and  $c_0 = 5.199$ . The values after cathodic polarization at 2.3 ma  $\text{cm}^{-2}$ , for 10 hr at 92°C in a

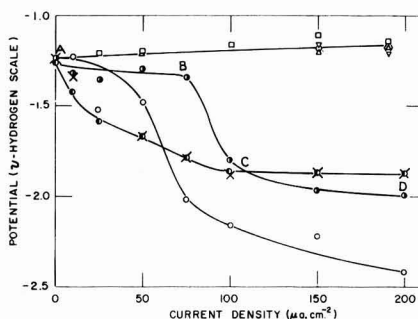


Fig. 4. Anodic polarization curve of magnesium in a 110 ppm NaCl solution: pH = 10 to 9; square, 25°C, diamond, 58°C; triangle, 75°C; inverted triangle, 92°C. Cathodic polarization curves of magnesium in 110 ppm NaCl solution: pH = 10 to 9; circle, 25°C; circle, right half solid, 58°C; circle, left half solid, 75°C; X, 92°C.

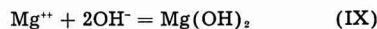
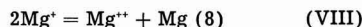
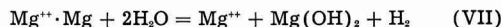
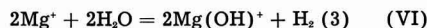
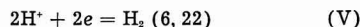
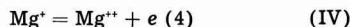
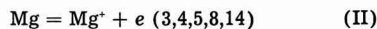
boric acid-sodium hydroxide solution with 110 ppm NaCl buffered at pH = 9.25 are  $a_0 = 3.202$  and  $c_0 = 5.200$ . The change in the parameters is within experimental error.

A Mg electrode in the form of a tube with the immersed end closed and the open end joined to a gas buret was cathodically polarized at 92°C in a 110 ppm NaCl solution. No passage of  $\text{H}_2$  through the Mg was observed.

## Discussion

### Anodic Behavior of Magnesium

A tentative mechanism for the anodic oxidation of Mg including secondary reactions is:



Reaction (III) is energetically possible; the bond energy of  $\text{Mg}^{++} \cdot \text{Mg}$  would probably be about equal to the heat of sublimation of Mg (ca. 42 kcal mole<sup>-1</sup>

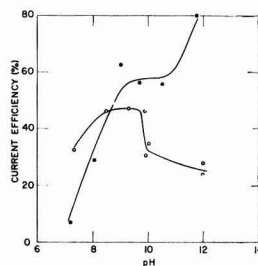


Fig. 5. Dependence of current efficiencies (%) of magnesium anodes polarized at 500  $\mu\text{a cm}^{-2}$  on the pH: open circle, ca. 25°C; solid circle, 75°C.



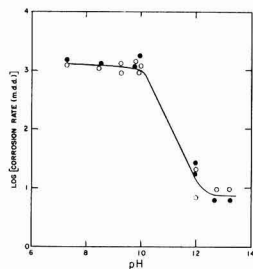


Fig. 6. Dependence of log [corrosion rate (mdd)] of magnesium cathodes polarized at  $500 \mu\text{a cm}^{-2}$  and nonpolarized specimens on the pH at  $25^\circ\text{C}$ ; open circle, cathodes; solid circle, local corrosion.

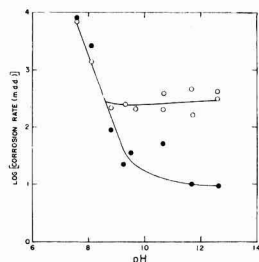


Fig. 7. Dependence of log [corrosion rate (mdd)] of magnesium cathodes polarized at  $500 \mu\text{a cm}^{-2}$  and nonpolarized specimens on the pH at  $75^\circ\text{C}$ ; open circle, cathodes; solid circle, local corrosion.

at  $25^\circ\text{C}$ ). Reaction (V) corresponds to the cathodic reaction of local corrosion on the anode. The reaction of  $\text{Mg}^+$  and  $\text{Mg}^{++}\cdot\text{Mg}$  with water is written purely formally in Eqs. (VI) and (VII), respectively. Monovalent Mg would be expected to have a short life time somewhat comparable to that of a free radical; the relatively long-lived reducing activity of the anolyte observed by Kleinberg, *et al.*, (3) is probably due to  $\text{Mg}^{++}\cdot\text{Mg}$  or colloidal Mg.  $\text{Mg}_s$  represents undermined Mg.

An expression may be derived for the anodic current efficiency of Mg in terms of the rates of the reactions postulated in the mechanism. Assuming Faraday's laws and a homogeneous current density over the entire anode for the electrochemical reactions.

$$\text{C.E. (\%)} = 100/[1 + (i_2 + i_3 + i_6 + i_s - i_4)/i_T] \quad (\text{XI})$$

where

$$i_T = i_1 + i_2 + i_3 + i_4 - i_5 \quad (\text{XII})$$

$i_T$  is the total external current in amperes;  $i_1$ ,  $i_2$ ,  $i_3$ ,  $i_4$ , and  $i_5$  are the currents due to the reactions (I), (II), (III), (IV), and (V), respectively.  $i_s/i_T$  is defined as the ratio of the weight loss due to undermining to the weight loss at an anode with 100% current efficiency. Magnesium metal formed by Eq. (VIII) would not effect Eq. (XI). Assuming a steady-state concentration of monovalent Mg and a uniform concentration of ions throughout the solution:

$$i_s - i_4 = FR \quad (\text{XIII})$$

and

$$\text{C.E. (\%)} = 100/[1 + (i_2 + i_3 + i_6 + FR)/i_T] \quad (\text{XIV})$$

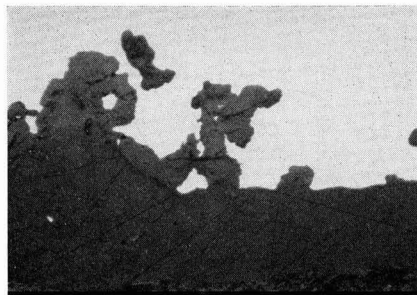


Fig. 8. Metallographic cross section of magnesium anode: polarization current =  $100 \mu\text{a cm}^{-2}$ ; temperature =  $75^\circ\text{C}$ ; time = 7 days; solution = 110 ppm NaCl. Magnification 150X before reduction for publication.

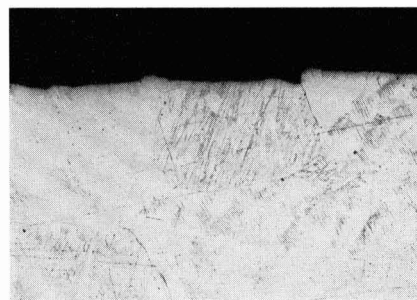


Fig. 9. Metallographic cross section of magnesium electrode demonstrating acid attack, etched. Magnification 150X before reduction for publication.

$F$  (coulombs) is the Faraday constant and  $R$  (moles  $\text{sec}^{-1}$ ) is the sum of the rates of disappearance of monovalent Mg by solution reactions.

At very low pH's and current densities the rate of the anodic dissolution of Mg which supplies external current ( $i_T$ ) is small compared to the rate of local corrosion ( $i_s$ ). This explains the experimental facts that the current efficiency is an increasing function of the current density and of pH in the low ranges (Fig. 2 and Fig. 5). Within experimental error the current efficiency is independent of the current density at high current densities, and, therefore,

$$(i_s + i_6 + i_s + FR)/i_T = C \quad (\text{XV})$$

where  $C$  is a constant which depends on temperature and pH. If reactions (II) and (III) are the only anodic reactions which occur, the minimum value of  $C$  is unity. Since  $C > 1$  in unbuffered solutions (Fig. 2), local corrosion and/or undermining ( $i_s$ ) must be important. Reaction (I) and/or reaction (IV) must be important since at  $75^\circ\text{C}$  in buffered solutions at high pH's  $C < 1$ . The thermodynamics of reaction (I) are indistinguishable from the thermodynamics of the process which takes place by the consecutive reactions (II) and (IV), but, of course, there is a marked difference in electrode kinetics.

Low current efficiencies may possibly be due to an enhancement of local corrosion by anodic polarization. Current efficiencies in buffered solutions are higher than in the unbuffered solution at

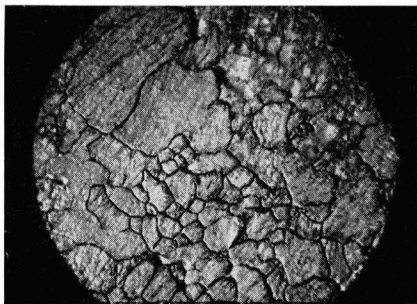


Fig. 10. Metallographic top view of magnesium cathode with corrosion products removed: polarization current =  $200 \mu\text{a cm}^{-2}$ ; temperature =  $58^\circ\text{C}$ ; time = 7 days; solution = 110 ppm NaCl. Magnification 50X before reduction for publication.

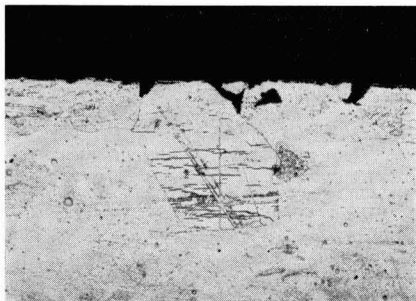


Fig. 11. Metallographic cross section of magnesium cathode with corrosion products removed, etched: polarization current =  $200 \mu\text{a cm}^{-2}$ ; temperature =  $58^\circ\text{C}$ ; time = 7 days; solution = 110 ppm NaCl. Magnification 150X before reduction for publication.

the same bulk pH at  $75^\circ\text{C}$  (compare Fig. 2 and Fig. 5). This may be considered to be experimental verification for Robinson's suggestion (6) that the corrosion rate at the anode is enhanced due to the excess acidity formed at the pits as a result of anodic polarization. However, this explanation is probably not satisfactory for buffered solutions.

An alternate theory may be suggested by considering the effect of buffered pH on the current efficiency. The nature and extent of attack on Mg is strongly affected by pH. An acid type of attack (Fig. 9) occurs at the Mg anodes and locally corroding specimens at pH's  $< 10$  at  $25^\circ\text{C}$  and at pH's  $< 9$  at  $75^\circ\text{C}$  without visible film formation; above these pH's a pitting type of attack occurs similar to that observed in unbuffered 110 ppm NaCl solution (Fig. 8) and thick white films of  $\text{Mg}(\text{OH})_2$  containing free Mg are formed. There is evidence for thin films of MgO and/or  $\text{Mg}(\text{OH})_2$  on Mg in acid solution, the mechanism of formation of which is obscure (11). The thick film of  $\text{Mg}(\text{OH})_2$  is probably formed by reaction (IX). Further corrosion of the magnesium in the  $\text{Mg}(\text{OH})_2$ -Mg film undoubtedly occurs. In strong NaCl solution the corrosion products were observed to flake off and fall to the bottom of the container. Gas evolution from the corrosion products at the bottom of the container continued for several minutes. Anodic passivity (C.E.  $> 100\%$ ) was observed at the higher pH's at room temperature and  $75^\circ\text{C}$ .

The formation of thick films of  $\text{Mg}(\text{OH})_2$ -Mg on anodically polarized Mg may possibly lead to an enhancement of the rate of local corrosion at the anode if it is assumed that: (a) the film on the anode,  $\text{Mg}(\text{OH})_2$ -Mg, is cathodic to the pits or anodic areas; and (b) the amount of Mg in the film, and, hence, the resistance of the film reaches a steady value which is proportional to the current density. The resistance of the film is therefore inversely proportional to the anodic current density, and the rate of corrosion at the anode is directly proportional to the current density. Thus, local corrosion could conceivably account for the sharp decrease in current efficiency at pH = 10 at room temperature (Fig. 5). Since the current efficiencies observed at room temperature are considerably lower than at the elevated temperatures, it must be assumed that at elevated temperatures the resistance between local cathodic and anodic areas is increased. This may be accomplished in two ways: (a)  $\text{Mg}(\text{OH})_2$  is less soluble at higher temperatures and stifling of the local corrosion at the anode would be more important; and (b) cathodic corrosion of the free Mg in the film would occur (Fig. 3). Shishakov (12) has observed that the film formed on Mg in boiling water is more protective than the film formed at room temperature.

It is not possible to ascertain the importance of undermining in the mechanism for the anodic oxidation of Mg. On comparison of Fig. 8 and Fig. 9 it can be seen that film formation enhances undermining of Mg at least on the macro scale. Dissolution of a Mg anode by cathodic corrosion at the higher temperatures and current densities may be important. Cathodic corrosion will be discussed in the next section.

The measured potential of the Mg anode which is about 1 v more cathodic than the equilibrium potential of reaction (I) can probably not be identified with the potential of any of the three remaining anodic reactions. The equilibrium potential of the process consisting of the consecutive reactions (II) and (IV) is the same as the equilibrium potential of reaction (I). As pointed out previously either reaction (I) or reactions (II) and (IV) must occur. Since large overpotentials are not usually associated with anodic processes involving metal ions (29), the measured potential is either a composite potential of local anodic and local cathodic areas on the anode or the measured potential contains a large ohmic potential drop contribution. The experimental potential cannot be identified with that of reaction (III) since this would entail large potential differences between the various crystal faces of Mg.

#### *Cathodic Behavior of Magnesium*

The salient facts of the cathodic polarization experiments are: (a) cathodic polarization inhibits the corrosion of Mg in 110 ppm NaCl solutions at  $25^\circ\text{C}$  and  $58^\circ\text{C}$  (Fig. 3); (b) at  $75^\circ$  and  $92^\circ\text{C}$  cathodic protection is not attained due to the occurrence of an intergranular type of cathodic corrosion (Fig. 10 and Fig. 11); (c) intergranular attack of cathodically polarized Mg occurs at pH's  $> 9$

at 75°C with formation of thick films of  $\text{Mg}(\text{OH})_2$  and acid attack (etching-type attack) without visible film formation occurs at  $\text{pH}'s < 9$  at 75°C and at  $\text{pH}'s < 10$  at room temperature on both unpolarized and cathodically polarized Mg; (d) the rate of intergranular cathodic corrosion is dependent on temperature and current density, and at 75°C is independent of pH at  $\text{pH}'s > 9$  (Fig. 7); (e) the rate of acid corrosion is dependent on temperature and pH and independent of cathodic current density at room temperature and 75°C (Fig. 6 and Fig. 7); (f) the lattice parameters of Mg are not significantly affected by cathodic polarization at 92°C; and (g) hydrogen produced at the cathode at 92°C does not diffuse readily through the Mg.

It is evident that under the experimental conditions studied in this work the mechanism of acid corrosion at room temperature and intergranular corrosion of cathodically polarized Mg are different; intergranular cathodic corrosion becomes significant only at elevated temperatures, whereas, the acid corrosion of Mg is quite appreciable at room temperature. Acid corrosion and intergranular corrosion on Mg cathodes probably occur simultaneously at elevated temperatures, although it appears that film formation greatly diminishes the acid corrosion relative to the intergranular corrosion. The mechanism for the acid dissolution of Mg has been studied extensively and is not discussed here (20-25).

The phenomenon of the intergranular cathodic corrosion of Mg may be interpreted in terms of the hydrogen embrittlement theory for steel (30, 31) with some modification. The hydrogen embrittlement theory for Mg may be based on the following assumptions: (a) hydrogen is occluded in Mg at the dislocations near the solution-metal interface by cathodization; (b) deep penetration of cathodic hydrogen into the Mg lattice does not occur (diffusion of hydrogen through Mg during cathodization was not observed and cathodization does not increase significantly the amount of interstitial hydrogen); and (c) the dislocations are "sprung" forming embrittled Mg at the solution-metal interface when the hydrogen pressure at the dislocation exceeds the elastic strength of Mg. The mechanically weakened lattice of Mg is subject to corrosion by mechanical undermining or by electrochemical corrosion. The degree of embrittlement and, hence, the rate of cathodic intergranular corrosion, would be dependent on temperature and current density.

The general shape of the cathodic polarization curves of Mg (Fig. 4) at room temperature and 58°C are similar to the cathodic polarization curves obtained for iron (32). AB represents depolarization by oxygen; CD represents evolution of hydrogen; and the current at B is the current required for cathodic protection (16). The data are insufficient to explain the absence of the inflection at B in the polarization curves at 75° and 92°C and the fact that the hydrogen overvoltage is considerably

lower at the higher temperature than that at room temperature. Probably, the contribution of the ohmic p.d. to the hydrogen overpotential at the elevated temperature is smaller.

#### Acknowledgment

The authors wish to express their appreciation to Mrs. A. F. Beck and Dr. L. D. Calvert for the x-ray results and to Mr. P. E. Beaubien for the metallographic work reported in this paper.

Manuscript received Aug. 1, 1957. This paper was prepared 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 1958 JOURNAL.

#### REFERENCES

1. A. Smits, *Z. Elektrochem.* **30**, 223 (1924).
2. S. Bodforss, *Z. Physik. Chem.*, **153**, 83 (1931).
3. M. D. Rausch, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, **76**, 363, 3622 (1954); **77**, 2093 (1955).
4. W. E. McEwen, J. Kleinberg, D. L. Burdick, W. D. Hoffman, and J. Y. Yang, *ibid.*, **78**, 4587 (1956).
5. P. Brouillet, I. Epelboin, and M. Froment, *Compt. rend.*, **239**, 1795 (1954).
6. H. A. Robinson, *Trans. Electrochem. Soc.*, **90**, 485 (1946); "Cathodic Protection, A Symposium," p. 104, N.A.C.E., Houston (1949).
7. H. A. Robinson and P. I. George, *Corrosion*, **10**, 182 (1954).
8. J. H. Greenblatt, *This Journal*, **103**, 539 (1956).
9. R. Faivre and A. Michel, *Compt. rend.*, **208**, 1008 (1939).
10. C. Brouchere, *J. Inst. Metals*, **71**, 131 (1943).
11. K. Huber, *This Journal*, **100**, 376 (1953).
12. N. A. Shishakov, *Zhur. Fiz. Khim.*, **26**, 358 (1952).
13. S. Yamaguchi, *J. Appl. Phys.*, **25**, 1437 (1954); *J. Chem. Soc. Japan*, **61**, 887 (1940).
14. W. Beetz, *Pogg. Ann.*, **27**, 115 (1866).
15. W. J. Müller and E. Nachtigall, *Monatsh.*, **69**, 1 (1936); *Korrosion u. Metallschutz*, **14**, 198 (1938).
16. U. R. Evans, L. C. Bannister, and S. C. Britton, *Proc. Royal Soc. (London)*, **A131**, 367 (1931).
17. E. H. Phelps, Thesis, Case Institute of Technology, Cleveland, Ohio (1955).
18. G. V. Akimov and I. L. Rozenfeld, *Compt. rend. acad. sci. U.R.S.S.*, **44**, 193; *Doklady Akad. Nauk, S.S.S.R.*, **44**, 211 (1944).
19. F. E. W. Wetmore, Private communication.
20. C. V. King and W. H. Cathcart, *J. Am. Chem. Soc.*, **59**, 63 (1937).
21. J. H. James, *ibid.*, **65**, 39 (1943).
22. G. E. Coates, *J. Inst. Metals*, **71**, 457 (1945).
23. A. B. Garret and R. R. Cooper, *J. Phys. and Colloid Chem.*, **54**, 437 (1950).
24. B. Roald and W. Beck, *This Journal*, **98**, 277 (1951).
25. E. J. Casey and R. E. Bergeron, *Can. J. Chem.*, **31**, 849 (1953).
26. *Int. Critical Tables*, **6**, 152 (1929).
27. H. T. S. Britton, "Hydrogen Ions," Vol. I, Chapman and Hall Ltd., London (1955).
28. R. G. Bates and V. E. Bower, *J. Research Nat. Bur. Standards*, **53**, 283 (1954).
29. A. Hickling, *Quarterly Revs. (London)*, **3**, 95 (1949).
30. C. A. Zapffe and C. E. Sims, *Am. Inst. Mining Met. Engrs.*, **145**, 225 (1941).
31. C. A. Zapffe, *Materials & Methods*, **32**, 74 (1950).
32. G. R. Hoey and M. Cohen, *Corrosion*, To be published.

# Investigations in the $\text{CuGaS}_2$ -ZnS and $\text{AgGaS}_2$ -ZnS Systems

E. F. Apple

Research Laboratory, General Electric Company, Schenectady, New York

## ABSTRACT

$\text{CuGaS}_2$  and ZnS form solid solutions over the entire range with some evidence for compound formation at 33 1/3 mole %  $\text{CuGaS}_2$ . Emission under 3650Å excitation shifts from green to red with increase in  $\text{CuGaS}_2$  concentration. Samples with more than 20%  $\text{CuGaS}_2$  do not luminesce at room temperature but, at  $-195^\circ\text{C}$ , fairly bright emission is observed with up to 95%  $\text{CuGaS}_2$ .  $\text{AgGaS}_2$  is soluble in ZnS to about 5-10 mole %, above which separation of  $\text{Ag}_2\text{S}$  is observed. Emission under 3650Å excitation shifts from the blue (0.01%  $\text{AgGaS}_2$ ) to yellow (10%  $\text{AgGaS}_2$ ).

The ternary sulfides,  $\text{CuGaS}_2$  and  $\text{AgGaS}_2$ , have the chalcopyrite structure which is closely related to the zinc blende structure of cubic ZnS (1). In these compounds, two different atomic species occupy equivalent lattice sites on the zinc blende lattice. In  $\text{CuGaS}_2$ ,  $a = 5.34\text{\AA}$  and  $c = 10.47\text{\AA}$  ( $c/a = 1.96$ ) while in  $\text{AgGaS}_2$ ,  $a = 5.74\text{\AA}$  and  $c = 10.26\text{\AA}$  ( $c/a = 1.79$ ) (2).

Because of the similarities in structure, unit cell dimensions, and bond type, the ternary sulfides may form solid solutions with ZnS. In such solid solutions, the ternary compounds would not only change the unit cell dimension of ZnS, but may also affect the observed luminescence in ZnS:Cu,Ga and ZnS:Ag,Ga phosphors. Cu and Ag are activators and Ga is a coactivator in normal ZnS phosphors with green and blue emission.

The solubility of these activators in ZnS is dependent on the presence of charge-compensating ions which usually function as coactivators (3). For instance, in ZnS:Cu with no chemical coactivator added, Froelich reported that only about  $4 \times 10^{-3}$  g-atoms Cu/mole ZnS is retained in the lattice after firing (4). In contrast, at least  $9 \times 10^{-3}$  g-atom Cu/mole ZnS is retained in the ZnS:Cu,Al phosphor with orange emission (5). Incorporation of the larger concentration of Cu in the latter case is possible because of the simultaneous incorporation of Al as  $\text{Al}_2\text{S}_3$ . In this phosphor, the Al was added to ZnS as an oxy-salt and converted to  $\text{Al}_2\text{S}_3$  during the firing process in  $\text{H}_2\text{S}$  at  $1100^\circ\text{C}$ - $1200^\circ\text{C}$ . It is questionable whether a large amount of  $\text{Al}_2\text{O}_3$  would be converted completely to  $\text{Al}_2\text{S}_3$  when fired in the presence of ZnS in an  $\text{H}_2\text{S}$  stream. Equimolar mixtures of ZnS and  $\text{Al}_2\text{O}_3$ , for instance, when so fired do not yield  $\text{ZnAl}_2\text{S}_4$ , the compound expected on complete conversion of the oxide to the sulfide. In all probability, addition of Al as the oxide or oxy-salt limits the solubility of Cu because of incomplete conversion to  $\text{Al}_2\text{S}_3$ . However, if the activator and coactivator are added as the ternary sulfide, the oxide conversion is circumvented. Further, activator and coactivator are added in exactly stoichiometric amounts in a form which facilitates incorporation in the lattice.

It is the purpose of this paper to report results of studies in the systems  $\text{CuGaS}_2$ -ZnS and  $\text{AgGaS}_2$ -ZnS. Of special interest will be the structural data, limits of solubility, and luminescent properties. In these systems the concentrations of Cu or Ag in ZnS far exceed those reported in the literature, and with the increased concentrations of activators incorporated new luminescent properties are observed.

## Experimental Results

### $\text{CuGaS}_2$ -ZnS System

A stoichiometric mixture of  $\text{Cu}_2\text{S}$  (made from 99.999% Cu) and  $\text{Ga}_2\text{S}_3$  (made from 99.97%  $\text{Ga}_2\text{O}_3$ ) was heated in a sealed, evacuated ampoule for 12 hr at  $900^\circ\text{C}$ . The body color of the mixture changed from gray to orange as a result of this firing process and an x-ray diffraction pattern of the powder indicated that  $\text{CuGaS}_2$  had formed (diffraction lines due to  $\text{Cu}_2\text{S}$  or  $\text{Ga}_2\text{S}_3$  were absent).

Weighed mixtures of  $\text{CuGaS}_2$  and ZnS (G.E. luminescent grade) were ground and ballmilled together and then fired at  $975^\circ\text{C}$  for 1 hr in  $\text{H}_2\text{S}$ . [The  $\text{H}_2\text{S}$  used throughout this work was passed through a  $\text{Ba}(\text{OH})_2$  solution, then through drying columns containing silica gel and phosphorus pentoxide, and finally through a trap held at  $-50^\circ\text{C}$  before coming in contact with the sample.] The entire range of concentrations from 0.01 mole % to 99.9 mole %  $\text{CuGaS}_2$ \* was covered. The body color changed from near-white in the 0.01% sample through green to orange in the 30-40% region; between 50-90% it went from orange to green; above 90% the body color was orange. In no case was free  $\text{Cu}_2\text{S}$  observed or did the powders have a dark body color.

X-ray diffraction patterns of the powders indicate that the structure is cubic in mixtures with up to and including 40%  $\text{CuGaS}_2$ . The unit cell dimension, as plotted in Fig. 1, decreases from 5.404Å (pure ZnS) to 5.350Å (40%  $\text{CuGaS}_2$ ) with Vegard's law being obeyed approximately. Diffraction lines characteristic of tetragonal  $\text{CuGaS}_2$  are absent in this range and it is concluded that  $\text{CuGaS}_2$  and ZnS are miscible up to and including 40 mole %  $\text{CuGaS}_2$ .

\* Concentrations throughout paper are in mole %  $\text{CuGaS}_2$  or  $\text{AgGaS}_2$  unless otherwise indicated.

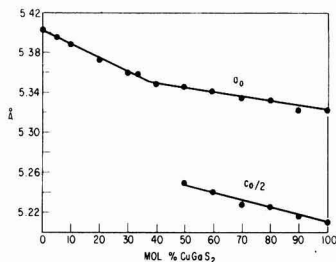


Fig. 1. Unit cell dimensions in the system ZnS-CuGaS<sub>2</sub>

Above 40% CuGaS<sub>2</sub>, the structure is tetragonal with the  $a_0$  and  $c_0$  dimensions decreasing nearly linearly with increase of CuGaS<sub>2</sub>. The  $c/a$  ratio remains about the same and in all probability solid-solution formation occurs throughout the tetragonal region also. It is thus concluded from the x-ray data and also from the orderly, if not continuous, change in physical properties throughout, that CuGaS<sub>2</sub> and ZnS are completely miscible.

Samples with 20% and less CuGaS<sub>2</sub> luminesce at room temperature under 3650Å excitation (which excitation appears to be in the optimum wavelength region). The emission moves from the green into the red and, in general, the spectral distribution of emission at room temperature broadens and the brightness drops with increasing CuGaS<sub>2</sub> content. No visual afterglow occurs when excitation is removed in all samples except 0.01% CuGaS<sub>2</sub> where a long bright green afterglow is observed. Emission spectra at room temperature are shown in Fig. 2 and peak values are plotted in Fig. 3. At -195°C, luminescence is observed under 3650Å excitation in all samples in the series including CuGaS<sub>2</sub>, in which the spectral distribution of emission extends beyond 7000Å and is too weak to record accurately on the spectroradiometer used. As indicated in Fig. 3, the emission peak at -195°C shifts from the characteristic green in low CuGaS<sub>2</sub> samples to a maximum wave length in the 30-40% range with the peak in the 33 1/3% sample being shifted abnormally to above 7000Å. Above 40% the peak shifts back gradually to shorter wave lengths until at 70% CuGaS<sub>2</sub> a sudden shift to a longer wave length is observed. Samples with 70% and above show evidence of two emission bands and the peaks of these bands are in fact resolved in the 90% sample as shown in Fig. 4. The half-width of the emission spectra at -195°C shows a minimum in the 30-40% region.

Thermoluminescent experiments indicate the presence of two principal glow peaks in all samples in the series. After excitation at -195°C with a BH-4 lamp and using a 10°/min heating rate, one glow peak falls in the -160° to -180°C region and the other peak occurs at -90° to -110°C.

Cathodoluminescence in samples with more than 1% CuGaS<sub>2</sub> is very weak and the spectral distribution of emission is about the same as that for 3650Å excitation.

The diffuse reflectivity, (see Fig. 5) moves to longer wave lengths with increasing CuGaS<sub>2</sub> content. The reflectivity edge shows a maximum in wave length in the 30-40% region with the edge in

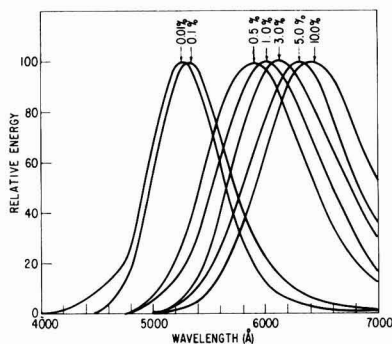


Fig. 2. Emission spectra (normalized) of ZnS-CuGaS<sub>2</sub> at room temperature under 3650Å excitation. Percentages indicate CuGaS<sub>2</sub> content. Samples fired in H<sub>2</sub>S for 1 hr at 975°C.

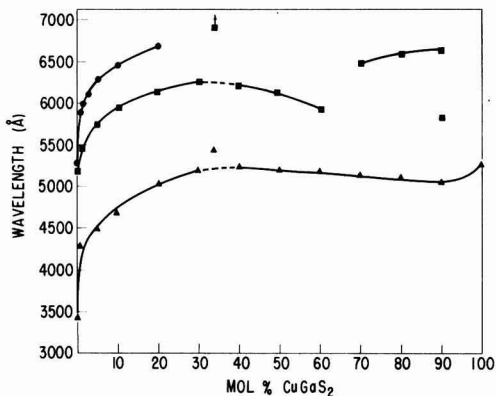


Fig. 3. Emission peak at room temperature and at -195°C, and diffuse reflectivity in ZnS-CuGaS<sub>2</sub> system. Circle, emission peak at room temperature; square, emission peak at -195°C; triangle, diffuse reflectivity (10% R reference).

the 33 1/3% CuGaS<sub>2</sub> sample being at a longer wavelength range than that of pure CuGaS<sub>2</sub>. Change in diffuse reflectivity and peak emission at -195°C closely parallel each other as shown in Fig. 3. Ten per cent reflectivity is used as the point of reference.

Firing the samples containing less than 20% CuGaS<sub>2</sub> in H<sub>2</sub>, N<sub>2</sub>, S<sub>2</sub>, or in sealed, evacuated tubes instead of in H<sub>2</sub>S has no effect on the spectral distribution of emission or the diffuse reflectivity. However, firing in O<sub>2</sub> or air for a few minutes causes the samples to darken and deadens the luminescence in most cases. Presumably, oxygen destroys the solid solution by precipitating Ga as Ga<sub>2</sub>O<sub>3</sub> thus lowering the solubility of Cu<sub>2</sub>S in ZnS. The temperature of preparation or, more specifically, the crystal structure of the lattice has a marked effect on the luminescent properties. Samples with 1 to 10% CuGaS<sub>2</sub> prepared at 1150°C in H<sub>2</sub>S have the hexagonal structure and give a dim orange-red emission under 3650Å excitation as compared to the yellow to red emission of the samples fired at 975°C. In the 20% sample fired at 1150°C, the structure is cubic and the brightness and spectral distribution of emission are about the same as in the corresponding sample fired at 975°C. Structure, apparently, is very important in the luminescent processes involved, a



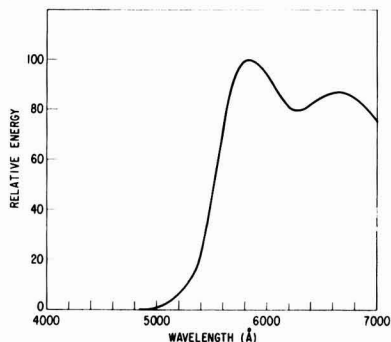


Fig. 4. Emission spectra of 0.1 ZnS·9CuGaS<sub>2</sub> at -195°C under 3650Å excitation.

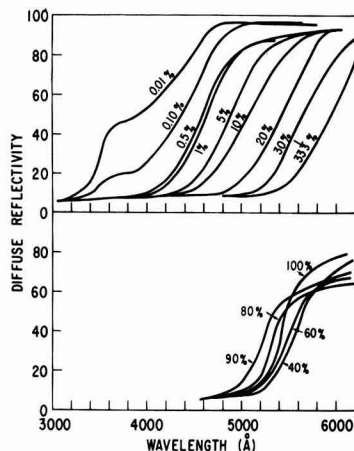


Fig. 5. Diffuse reflectivity spectra of ZnS-CuGaS<sub>2</sub>.

fact which is observed even in the 0.01% CuGaS<sub>2</sub> material.

ZnS:0.01% CuGaS<sub>2</sub> prepared in H<sub>2</sub>S or in a sealed, evacuated ampoule at 975°C shows a green emission under 3650Å excitation at room temperature and a blue-green emission at -195°C. However, the same material fired at 1150°C under either condition gives a green emission at room temperature but a red emission at -195°C (see Fig. 6). In the first case, the structure is cubic and in the latter case, it is hexagonal. As will be discussed later, this effect of structure on emission is observed in a fairly large number of systems under study at the present time.

#### AgGaS<sub>2</sub>-ZnS System

AgGaS<sub>2</sub> was made by heating a stoichiometric mixture of Ag<sub>2</sub>S and Ga<sub>2</sub>S<sub>3</sub> in an evacuated, sealed tube at 900°C for 12 hr. The product obtained was light green in color. Mixtures of ZnS and up to 20 mole % AgGaS<sub>2</sub> were fired in H<sub>2</sub>S at 900°C for 1 hr. In samples with over 5% AgGaS<sub>2</sub>, black specks were observed throughout the fired material indicating separation of Ag<sub>2</sub>S. For this reason, the study was terminated at 20 mole %.

Using 3650Å excitation, photoluminescence is observed at room temperature over the entire range studied. The emission shifts from the blue into the

yellow as the AgGaS<sub>2</sub> content is increased. Too, the spectral distribution of emission widens and the brightness decreases. Emission spectra are shown in Fig. 7. At -195°C, the emission peak of a given sample shifts 400-500Å to shorter wave lengths as is shown in Fig. 8 and the luminescence becomes much brighter than at room temperature. Cathodoluminescence is observed in all samples, but the peak emission occurs 50-100Å shorter in wave length than that in photoluminescence.

Diffuse reflectivity spectra shown in Fig. 9 also shift to longer wave length with increasing AgGaS<sub>2</sub> content. Most of the samples containing Ag were light sensitive, and darkened on exposure to sunlight.

With 5% and below AgGaS<sub>2</sub>, the structure in the system is cubic (in samples prepared at 900°C), it is a mixture of cubic and hexagonal in the 10% region, and is hexagonal in the 20% sample. This change in structure is explained by assuming a solid solution of Ga<sub>2</sub>S<sub>3</sub> and ZnS forms in the region where Ag<sub>2</sub>S precipitates. Such a solid solution of Ga<sub>2</sub>S<sub>3</sub> in ZnS is hexagonal in this concentration range when prepared at 900°C (6).

As in ZnS:CuGaS<sub>2</sub> a marked effect of structure on luminescent properties was observed. In ZnS:0.01% AgGaS<sub>2</sub> prepared in H<sub>2</sub>S at 900°C, the emission under 3650Å excitation both at room temperature and at -195°C is blue. However, the emission

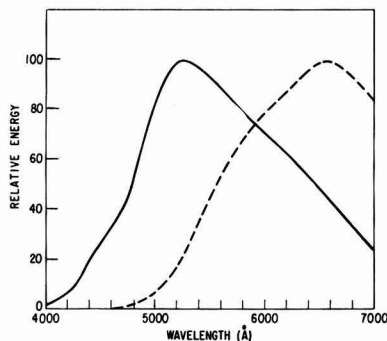


Fig. 6. Emission spectra (normalized) of ZnS:0.01% CuGaS<sub>2</sub> using 3650Å excitation. Sample fired at 1150°C in H<sub>2</sub>S for 1 hr. — Room temperature; - - - - -195°C.

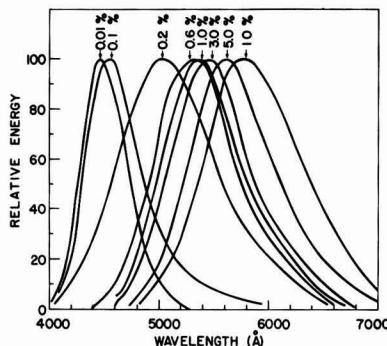


Fig. 7. Emission spectra (normalized) of ZnS-AgGaS<sub>2</sub> at room temperature under 3650Å excitation. Percentages indicate AgGaS<sub>2</sub> content. Samples fired in H<sub>2</sub>S for 1 hr at 900°C.

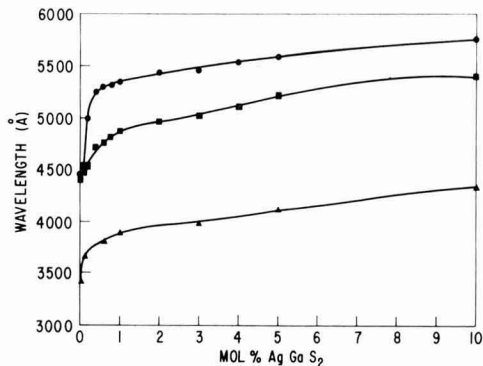


Fig. 8. Emission peak at room temperature and at  $-195^{\circ}\text{C}$ , and diffuse reflectivity in  $\text{ZnS-AgGaS}_2$  system. Circle, emission peak at room temperature; square, emission peak at  $-195^{\circ}\text{C}$ ; triangle, diffuse reflectivity (10% R reference).

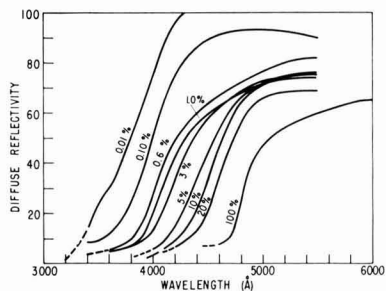


Fig. 9. Diffuse reflectivity spectra of  $\text{ZnS-AgGaS}_2$ .

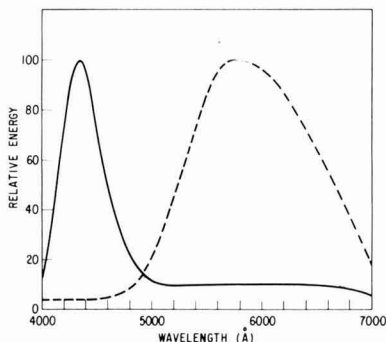


Fig. 10. Emission spectra (normalized) of  $\text{ZnS:0.01\% AgGaS}_2$  using  $3650\text{\AA}$  excitation. Sample fired at  $1150^{\circ}\text{C}$  in  $\text{H}_2\text{S}$  for 1 hr. — Room temperature; - - -  $-195^{\circ}\text{C}$ .

of a sample fired in  $\text{H}_2\text{S}$  at  $1150^{\circ}\text{C}$  is blue at room temperature but yellow at  $-195^{\circ}\text{C}$  as shown in Fig. 10. The structure in the sample fired at  $900^{\circ}\text{C}$  is cubic and it is hexagonal in the one fired at  $1150^{\circ}\text{C}$ .

### Discussion

Two compounds whose structures are similar sometimes are miscible over a wide concentration range. For instance,  $\text{InAs}$  and  $\text{InP}$  form mixed crystals in which the relations between the unit cell dimensions or energy gap (optical) and the composition parameter are linear (7).

$\text{CdS}$  and  $\text{ZnS}$  form a like series of solid solutions, in which the diffuse reflectivity spectra shifts from

that of pure  $\text{ZnS}$  to  $\text{CdS}$  as  $\text{CdS}$  substitutes in the lattice.  $\text{CdS}$  substitution in the  $\text{ZnS:Ag,Cl}$  phosphor shifts the emission spectra uniformly from blue into the red (8).

In the  $\text{ZnS-CuGaS}_2$  system, however, some of the physical properties are not a linear function of composition even though structural data indicate solid-solution formation over the entire range. Maxima in the wave lengths of the diffuse reflectance edge and peak emission (under  $3650\text{\AA}$  excitation) and a minimum in the half-width of emission spectra occur in the 30-40%  $\text{CuGaS}_2$  region. This suggests the possibility of compound formation or ordering in the structure in this region. In fact, at 33 1/3%  $\text{CuGaS}_2$ , where marked shifts in emission spectra and diffuse reflectance are observed, the compound  $\text{Zn}_2\text{CuGaS}$ , may form, in which case each S atom would be surrounded by two Zn atoms, one Cu atom, and one Ga atom. However, such an ordered arrangement would give a tetragonal structure whereas the structure of the 33 1/3% sample is cubic. Unfortunately compound formation or ordering in this system is difficult to detect by ordinary x-ray diffraction methods because of the similarity in atomic scattering factors of Cu, Zn, and Ga. However, the extreme sharpness of the  $\text{K}\alpha_1$  and  $\text{K}\alpha_2$  lines in the back reflection region of the x-ray diffraction pattern of 33 1/3%  $\text{CuGaS}_2$  indicates virtually no tetragonal distortion. Superstructure lines are not observed in the diffraction pattern even with very long exposure times. The compound, if formed, must have a pseudocubic structure ( $c/a = 2.00$ ).

Above 40%  $\text{CuGaS}_2$ , the diffuse reflectivity shifts to shorter wave lengths and the emission spectra become a composite of two emission bands. X-ray data shows a linear decrease in tetragonal cell dimensions in this region. Again compound formation or ordering would be difficult to detect by x-ray diffraction methods.

It should be pointed out that some solid solutions between two compounds exhibit properties which are not linear with composition. For instance,  $\text{GaP}$  and  $\text{GaAs}$  form mixed crystals but the relationship between the energy gap  $\Delta E$  and the composition parameter is not linear. This has been attributed to a difference in band structures for  $\text{GaAs}$  and  $\text{GaP}$  (7). Such a difference in band structures in  $\text{ZnS}$ ,  $\text{Zn}_2\text{CuGaS}$ , and  $\text{CuGaS}_2$  would explain the observed variation in properties throughout the  $\text{ZnS-CuGaS}_2$  system.

The nature of the luminescent systems in  $\text{ZnS}$  phosphors has received considerable attention (9). In these phosphors, the activator (Cu, Ag, Au) and coactivator (Cl, Al, Ga, etc.) concentrations are in the  $10^{-4}$  g-atoms/mole  $\text{ZnS}$  range where departures from random distribution of the added impurities undoubtedly affect the luminescent properties. In fact the observed photoluminescent properties, including edge emission, in  $\text{ZnS}$ -type phosphors can be explained by an associated donor-acceptor luminescent center (10). It is thought that an understanding of the luminescent processes in the  $\text{ZnS-CuGaS}_2$  (above 0.1%) system where Cu and Ga are by necessity highly associated may lead to a better

understanding of the activator system in normal ZnS phosphors.

A comparison of emission under 3650Å excitation with Froelich's yellow- and orange-emitting ZnS phosphors (containing up to about  $9 \times 10^{-8}$  g-atom Cu/mole ZnS and  $5 \times 10^{-9}$  g-atom Al/mole ZnS) shows that ZnS:CuGaS<sub>2</sub> has about the same spectral distribution of emission as its ZnS:Cu,Al counterpart (5). This would indicate that the emission is relatively independent of the Group III element but apparently is due to levels introduced by Cu,† S or Zn vacancies are probably not involved in the luminescent process since preparation of a particular sample in reducing (H<sub>2</sub>, N<sub>2</sub>) or oxidizing (S<sub>2</sub>) atmospheres give identical emission spectra.

Above 40% CuGaS<sub>2</sub>, where the system is tetragonal, the Zn atoms have two choices for substitution, either in place of a Cu atom or for a Ga atom. In the former case Zn will be an electron donor and in the latter case it will have acceptor properties. These two different substitutions may give rise to levels producing the two emission bands observed in this part of the series. A preferential substitution by Zn on one type of lattice site would be evidenced by changes in relative intensities of the two emission bands.

In view of the complete miscibility of CuGaS<sub>2</sub> in ZnS, it is rather striking that the solubility of AgGaS<sub>2</sub> is limited to 5-10 mole %. Certainly size considerations of Ag alone could not preclude a greater solubility since CdS has been shown to be soluble in ZnS, and Cd and Ag are similar in size. As was mentioned earlier, the unit cell dimension ratio  $c/a$  in AgGaS<sub>2</sub> is 1.79 indicating a greater distortion than is observed in CuGaS<sub>2</sub> ( $c/a = 1.96$ ). This greater deviation from pseudocubic ( $c/a = 2.00$ ) may lower the solubility of AgGaS<sub>2</sub> in ZnS. Ga<sub>2</sub>S<sub>3</sub> is completely miscible in ZnS and, in contact with AgGaS<sub>2</sub>, would form a solid solution with ZnS when the concentration limit of the ternary sulfide is exceeded.

In the 0.01-10% AgGaS<sub>2</sub> range, uniform changes in properties such as emission and diffuse reflectance are observed. It appears from the photoluminescent spectra that the longest wave-length emission at room temperature in this system peaks at 5800-5900Å. The effect of trace impurities in the AgGaS<sub>2</sub> starting material must be considered in evaluating the spectra. The copper content of the AgNO<sub>3</sub> used in preparation of Ag<sub>2</sub>S was about 10<sup>-4</sup> wt % which corresponds to Cu contents in the AgGaS<sub>2</sub>-ZnS system studied of approximately 10<sup>-8</sup> to 10<sup>-7</sup> g-atom Cu/mole ZnS. This impurity may contribute slightly to the green emission observed in some samples, but several factors indicate that the over-all emission is a function of something other than Cu. First, the phosphorescence is very weak and of short duration in comparison to the long afterglow observed in, for example, ZnS:0.01%CuGaS<sub>2</sub>. Second, Cu present in such a low concentration as 10<sup>-8</sup> g-atom/mole ZnS would

give rise to blue or green emission only, whereas yellow emission is observed in the ZnS-AgGaS<sub>2</sub> system. For these reasons the observed luminescence is thought to arise from Ag and Ga impurities probably in highly associated configurations.

Of particular interest in the study of the AgGaS<sub>2</sub>-ZnS system is the observation of the effect of structure on the emission spectra of the 0.01% sample. When fired in H<sub>2</sub>S or in a sealed, evacuated tube at 1000°C or below, the normal blue emission (under 3650Å excitation) is observed both at room temperature and at -195°C. However, when the same starting material is fired at 1050°C or above, the emission is blue at room temperature but yellow at -195°C. A similar shift from green to orange-red is observed in the ZnS-0.01% CuGaS<sub>2</sub>. In fact, shifts due to structure changes have been observed in a number of systems including ZnS:0.01% CuInS<sub>2</sub>, ZnS:0.01% Ag-InS<sub>2</sub>, ZnS:0.01% Au,In, and ZnS:0.005% Ga<sub>2</sub>S<sub>3</sub>. In the systems containing In, the spectral shifts are observed at room temperature. The results of these studies will be included in a future communication. Suffice it to mention here that the effect is dependent on the crystal structure of the host lattice, ZnS, is reversible with change in structure from cubic to hexagonal or hexagonal to cubic, and is independent of firing atmosphere. It is thought that this effect of structure on luminescence may be related to a change in association of activator and coactivator in the ZnS host lattice.

#### Acknowledgments

The author wishes to acknowledge the assistance given him by the following: Mr. A. A. Carlson for preparation of some of the samples used; Miss G. P. Lloyd and Dr. F. J. Studer for the optical measurements; Mr. F. C. Mostek and Dr. P. D. Johnson for the thermoluminescent measurements.

Manuscript received Nov. 7, 1957. This paper was prepared for delivery before the Washington Meeting, May 12-16, 1957.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1958 JOURNAL.

#### REFERENCES

1. A. F. Wells, "Structural Inorganic Chemistry," p. 403, Oxford Press, London (1950).
2. H. Hahn, G. Frank, W. Klinger, A. Meyer, and G. Störger, *Z. anorg. u. allgem. Chem.*, **271**, 153 (1953).
3. F. A. Kröger and J. Dikhoff, *Physica*, **16**, 297 (1950).
4. H. C. Froelich, *This Journal*, **100**, 280 (1953).
5. H. C. Froelich, *ibid.*, **100**, 496 (1953).
6. H. Hahn, G. Frank, W. Klinger, A. Störger, and G. Störger, *Z. anorg. u. allgem. Chem.*, **279**, 260 (1955).
7. O. G. Folbreth, *Z. Naturforsch.*, **10a**, 502 (1955).
8. S. Lasof, R. Shrader, and H. Leverenz, "Preparation and Characteristics of Solid Luminescent Materials," p. 224, John Wiley & Sons, Inc., New York (1946).
9. See, for instance: J. S. Prener and F. E. Williams, *This Journal*, **103**, 342 (1956); R. Bowers and N. T. Melamed, *Phys. Rev.*, **99**, 1781 (1955); H. A. Klasens, *This Journal*, **100**, 72 (1953).
10. J. S. Prener and F. E. Williams, *Phys. Rev.*, **101**, 1427 (1956).

† It should be pointed out that ZnS:CuInS<sub>2</sub> does not give the same spectral distribution of emission as its ZnS:Cu,Al or ZnS:CuGaS<sub>2</sub> counterpart.

# The Effect of Impurities on the Plaque Brightness of a 3000°K Calcium Halophosphate Phosphor

A. Wachtel

Research Department, Westinghouse Lamp Division, Bloomfield, New Jersey

## ABSTRACT

The killing action of 27 elements has been investigated at 1, 10, 100, 1000, and 10,000 ppm addition to a specially purified 3000°K calcium halophosphate phosphor mix. At 1% addition, the observed reduction in output increases in the order: Al, Zr, Ce, La, Pb, Y, In, Sm, Cs, S, Pr, Nd, Na, Ag, Sn, W, Si, Mo, U, Ga, Cr, Ni, Fe, Cu, Co, V, and Ti. In the neighborhood of 100 ppm, the first five elements listed showed a slight enhancing effect. None of the elements tested had an appreciable effect on the color of the fluorescence, except where killing of the luminescence became very pronounced. Purification of chemicals for preparation of the unfired mix involved difficulties with respect to Fe and was more successful with certain organic reagents. The use of capped silica tubes enabled firings with a reproducibility of  $\pm 0.3\%$ .

In view of the widespread use of calcium halophosphate phosphors in the fluorescent lamp industry, it appeared desirable to obtain practical limits governing the permissible impurity content of commercial raw materials. Some previous publications (1,2) dealing with calcium halophosphate phosphors in a more general manner indicate the necessity of maintaining a certain degree of purity, but no specific information with respect to the individual effects of a large number of possible killers could be found.

While it is understood that, for practical purposes, only the performance of the phosphor in lamps is of interest, it is also known that the laborious and somewhat less reproducible nature of lamp testing may be due to factors other than intrinsic phosphor performance under simple conditions of 2537Å excitation in air. Thus, the measurement of plaque brightness was believed to be capable of yielding more fundamental information, as well as of enabling the testing of a larger variety of impurity additions. Inasmuch as one may safely assume that an appreciably impaired plaque output of a phosphor will be similarly reflected in the zero-hour performance of a fluorescent lamp made with this phosphor, this type of investigation could be employed to effect a considerable elimination of samples for future lamp testing. This study was undertaken mainly for this purpose and involves only the plaque output of the calcium halophosphate phosphors.

## General Considerations

*Composition of the unfired mix.*—Inasmuch as at the time at which this project was undertaken, some increased demand for 3000°K phosphor was anticipated a 3000°K (Warm White) formulation was

chosen. Its composition before firing, exclusive of  $\text{CO}_2$  and residual traces of  $\text{H}_2\text{O}$ , is shown below:

CaO	44.29%
$\text{P}_2\text{O}_5$	41.87
$\text{SrCl}_2$	3.74
$\text{CaF}_2$	6.02
Mn (as metal)	1.67
$\text{Sb}_2\text{O}_3$	2.41

Since the normal "white" halophosphate compositions differ from each other only in minor respects, it was assumed that the results obtained here would be reasonably representative for most similar species of this system.

*Nature of raw materials employed.*—In order to interpret small variations in phosphor output with confidence, a high degree of reproducibility of phosphor synthesis was desirable. The unfavorable influence of  $\text{H}_2\text{O}$  and reducing gases such as  $\text{NH}_3$  has already been pointed out by Jenkins, McKeag, and Ranby (1). Therefore, prefired  $\text{Ca}_2\text{P}_2\text{O}_7$  was preferred over the more usual  $\text{CaHPO}_4$ . Preliminary experiments have shown that reacting  $\text{CaCO}_3$  with  $(\text{NH}_4)_2\text{HPO}_4$  yields a coarser and more free-flowing material than if  $\text{H}_3\text{PO}_4$  is used as a source of  $\text{P}_2\text{O}_5$ . In spite of this, phosphor formation takes place as readily and yields similar products in each case. Incorporation of the Sb in a valence state greater than three (3) was shown to decrease the dependence of phosphor brightness on Sb addition. Since  $\text{Sb}_2\text{O}_3$  or  $\text{Sb}_2\text{O}_5$  was found to be gritty and difficult to admix with the rest of the ingredients, it was formed from  $\text{Sb}_2\text{O}_3$  on a  $\text{CaCO}_3$  carrier by heating to 500° and 600°C in air. Stronger heating was avoided to prevent the formation of calcium antimonates (4) with loss of  $\text{CO}_2$ , so as to avoid subsequent

chemical absorption of  $H_2O$  when small amounts of impurities are added in aqueous solution. The other ingredients ( $SrCl_2$ ,  $CaF_2$ ,  $MnCO_3$ ) were used in the usual form.

*Purity of raw materials.*—Purification procedures involving acid and alkaline  $H_2S$  precipitations (5) were found to work satisfactorily for most impurity elements originally present, except Fe. Using  $SrCl_2$  as a representative substance for most of the purification experiments, it was found that a great variety of procedures, including precipitation with collectors or firing in  $HCl-Cl_2$  mixtures, resulted in products whose chemically determined Fe content was very low and corresponded to the efficiency of the (chemical) purification procedures employed (which for the most part were based on known analytical reactions), while the spectrographically determined Fe content was invariably higher and of the order of 10–15 ppm. No satisfactory explanation for this phenomenon could be offered, except the hypothesis that part of the spectrographically detectable Fe is present in anionic, complexed, or otherwise less reactive form. In connection with this, it was interesting to note that nitrates or acetates were easier to free of Fe than chlorides.

The best results for Ca and Sr nitrates were obtained by partial precipitation with mixtures of ammonium carbonate and  $(NH_4)_2S$ , followed by diphenylthiocarbazon in excess with a  $Zn(NO_3)_2$  collector at pH = 8 to 8.5, filtration and chloroform extraction.  $Mn(CH_3COO)_2$  and ammonium carbonate (for preparation of Ca and Mn carbonates) were purified similarly, except for the use of 8-hydroxyquinoline instead of the dithizone, and the use of a  $Ca(NO_3)_2$  collector for ammonium carbonate, and no collector for the  $Mn(CH_3COO)_2$ .  $SbCl_5$  was slowly distilled at atmospheric pressure from a Pyrex retort (air cooled) and the distillate hydrolyzed and decomposed with doubly distilled  $H_2O$  and  $NH_3$  gas. Reagent grades of  $NH_4F$  (for reaction with  $CaCO_3$ ) and  $P_2O_5$  were found to be of sufficient purity.

It should be mentioned that inasmuch as Fe and Cu are known to be particularly harmful in calcium halophosphate phosphors, a very logical choice for the removal of these elements appeared to be ammonium-*N*-nitrosophenylhydroxylamine (cupferon). This turned out to be particularly ineffective with respect to Fe. Generally speaking, while the chemical detection of Fe is much more sensitive than the spectrographic method, the former appears to be limited to that portion of Fe which in most cases is easily removable. To a lesser degree, similar difficulties prevailed with Al. Thus, such parameters as solubility products of precipitates and known degrees of efficiency of separation and filtration techniques became almost meaningless and could not serve as more than an intuitive guide in this phase of the project.

#### Experimental Procedure

*Preparation of unfired phosphor mixes.*—The impurity elements were added in aqueous solution of concentrations adjusted so as to contain 50 mg, 5 mg, 0.5 mg, 0.05 mg, and 0.005 mg of the element

per 0.8 ml of solution. In order to avoid upsetting the metal:P:halide ratio of the phosphors, all elements of valence less than four were added as orthophosphates with enough  $HNO_3$  to maintain solubility. Where this was not possible, the stoichiometric equivalent of  $H_3PO_4$  was added separately with the nitrate. The introduction of Cl could not be avoided with Si (as  $SiCl_4$  in  $CCl_4$ ), so as to effect a higher degree of reactivity than that caused by the contact of the sample with the  $SiO_2$  firing container. Elements of valence greater than four were added as anions in the form of ammonium salts, together with the stoichiometric equivalent of  $Ca(NO_3)_2$  added separately.

The experimental procedure consisted of slurring 1 g aliquots of the unfired mix with 0.8 ml aliquots of impurity solution of each of the five concentrations respectively, drying, and dry mixing the residues with 4 g aliquots of the same unfired mix. Thus, 5 g samples with additions of 1, 10, 100, 1000, and 10,000 ppm impurity element were obtained. In the case of Si, the 1 g aliquot was first moistened with 80% alcohol so as to effect hydrolysis of the  $SiCl_4$  *in situ*. The precaution against  $H_2O$  could have been extended further by adding the solutions to the  $CaCO_3 + Sb_2O_3$  part of the mix only, followed by drying and then mixing with the rest of the phosphor components. However, preliminary tests showed this to be unnecessary.

*Phosphor firing.*—A particularly efficient closure which still permitted the dissipation of internal pressure consisted of 75 mm long tubes of 15 mm I.D., 17 mm O.D. transparent silica, closed at one end, and capped by similar tubes of 18 mm I.D., 20 mm O.D. Five such tubes containing 1, 10, 100, 1000, and 10,000 ppm impurity in the phosphor mix were arranged side by side in a covered silica firing pan and confined by fire brick so as to prevent movement of the caps due to internal pressure.

Two firings were conducted at  $1100^\circ C$  for 1 hr in air each. Between firings, the phosphors were screened through a 100 mesh screen. In duplicate series for each impurity tested, the tubes were aligned in reverse order in the firing pan. Using a uniform supply of an unfired calcium halophosphate mix, the reproducibility of brightness under 2537Å excitation of averaged duplicates was found to be of the order of  $\pm 0.3\%$ .

*Brightness measurements.*—The apparatus used was very similar to the one described by Butler and Mooney (6) and is shown in Fig. 1. A U-shaped low-pressure mercury lamp whose output was not filtered served as the exciting source; made of Vycor tubing, the ultraviolet component of the lamp output could be removed by insertion of a glass plate by means of which blank readings for each individual sample could be performed. The fluorescent light was measured by a Weston Photronic cell over which three color filters (blue, Viscor, amber) could be positioned by means of a sliding carriage. Three 50 mm diameter sample cells were also available for positioning in a sliding carriage, although only two of these cells were used here. The exposed area of the plaques could be varied by insertion of apertures of different diameters.



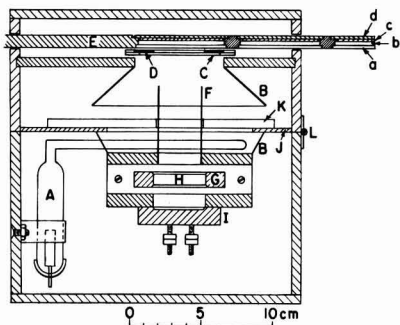


Fig. 1. Cross-sectional view of apparatus for measuring brightness of phosphor plaques: A, mercury arc lamp; B, aluminum reflectors; C, sliding carriage for apertures; D, E, sliding carriage with sample cells (a) quartz plate, (b) phosphor, (c) cardboard insert, (d) aluminum cover; F, aluminum tube; G, sliding carriage with color filters; H, I, photovoltaic cell; J, aluminum plate; K, glass plate inserted for blank readings; L, hinge. G and C slide perpendicular to the plane of the page.

The output of the Photronic cell was measured with a bridge circuit by means of the resistance selected to balance the cell output against that of a dry cell, using a multiple reflection galvanometer as null-indicator.

The measuring technique consisted in filling the first sample cell with a calcium halophosphate phosphor available in uniform supply, and placing the 1 ppm impurity sample in the second cell. The instrument was then normalized for this sample, and a reading was taken of cell No. 1. Subsequent samples were filled into cell No. 2 only, while cell No. 1 remained untouched and served only to restandardize the instrument at frequent intervals. Fatiguing of the Photronic cell became pronounced upon changing of color filters, requiring the establishment of equilibrium between individual readings. Individual blank readings were taken similarly after insertion of the glass plate to remove the 2537A radiation. All results reported here refer to the differences of total minus blank readings, normalized to 100 for the 1 ppm impurity samples.

Preliminary tests with a uniform supply of a calcium halophosphate phosphor indicated a reproducibility of brightness readings between subsequent charges of phosphor in any one sample cell of  $\pm 0.15\%$ .

### Results and Discussion

**Commonly occurring impurity elements.**—Figure 2 shows the effect of eight impurity elements (Fe, Cu, Ag, Na, Al, Si, Pb, and Sn) whose presence was usually detected in commercially available S.L. grade raw materials. It can be seen that only Fe exerted enough influence so that, at commonly occurring concentrations of about 15–30 ppm, appreciable interference may be expected. The usual concentration of Cu in S.L. grade raw materials is only of the order of 1–3 ppm. The effect of Fe and Cu at low concentrations as determined in separate trials is more clearly shown in Fig. 3. It should be mentioned that, while the emission of all phosphors was measured through each of the tricolor filters in the instrument, no appreciable effect on color was

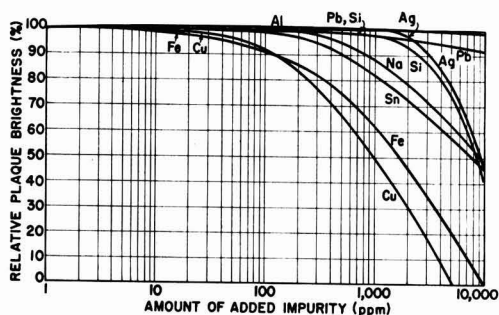


Fig. 2. Effect on brightness of eight commonly occurring impurity elements.

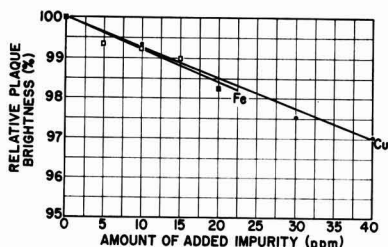


Fig. 3. Effect on brightness of Fe and Cu at low concentrations.

noted, except in cases of strong killing of the luminescence. Therefore, all figures show relative brightness only.

Enhancing effects which were sufficiently pronounced to be meaningful within the reproducibility of phosphor syntheses and measurements were noted only on Pb and Al. The results of separate trials with Pb and Al in the neighborhood of the observed emission maxima are shown in Fig. 4. The use of about 100 ppm Al has already been reported (7), while Pb (and Sn) have been used for the preparation of yellow or orange-emitting calcium halophosphates (8).

**The mechanism of enhancement by Al.**—While no investigations were made here pertaining to the mechanism (9) of the killer effect of Fe, it has been suggested (10) that Fe may enter the apatite lattice by charge compensation with alkalis, notably Na. Since the Fe and Na content of even highly purified raw materials cannot be neglected, one may expect that an appreciable concentration of Al may compete for charge compensation with such residual

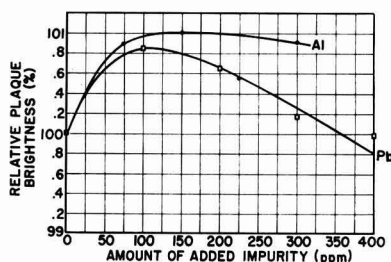


Fig. 4. Effect on brightness of Pb and Al in the neighborhood of enhancement maxima.

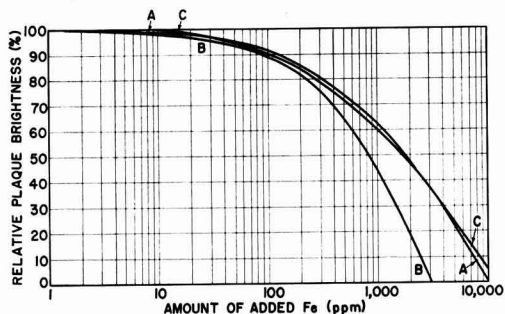


Fig. 5. Effect on brightness of Na or Al in combination with Fe. Curve A, Fe alone; curve B, Fe with 0.1% Na; curve C, Fe with 1.0% Al.

alkalies. This was investigated by firing variable concentrations of Fe in the presence of either 1% Al or 0.1% Na. A comparison with the effect of Fe alone is shown in Fig. 5, where all values have been normalized to 100 for the 1 ppm Fe addition. It can be seen that the effect of Fe was increased by the presence of Na. However, since, because of the strong effect of large concentrations of Na alone, not enough could be used to charge compensate more than about 0.24% Fe, the continued effect of Na above this Fe concentration cannot be explained. The effect of Al does not appear as pronounced, except in the neighborhood of 1% Fe, where the production of more than a very small background emission could be considered significant.

The behavior of presumably divalent Ni under similar conditions is shown in Fig. 6. Here again, Al and Na show opposite effects over most of the range, although at 1% Ni, neither Al nor Na appears to influence the output of the phosphor. It was felt that the results obtained here were inconclusive. It should also be mentioned that Wanmaker and Tak (11) have reported recently on mutually opposite effects of Na and Al on calcium halophosphates in the absence of heavy metal impurities.

*Trivalent elements other than Al.*—Examination of Fig. 7 shows that for the other trivalent impurities tried, with the exception of Ga which shows a rather sharp break around 0.1% and In which probably volatilized to a great extent, any enhancing effect noted (Ce, La) decreased with increasing

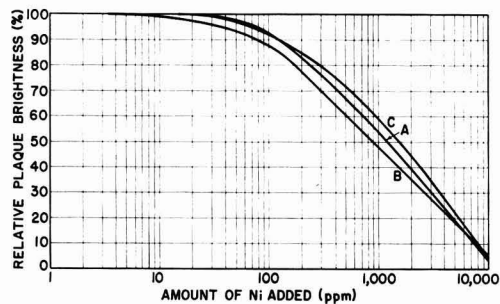


Fig. 6. Effect on brightness of Na or Al in combination with Ni. Curve A, Ni alone; curve B, Ni with 0.1% Na; curve C, Ni with 1.0% Al.

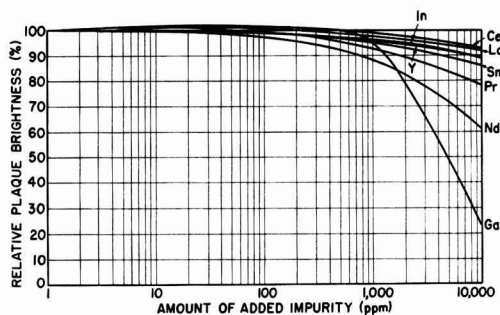


Fig. 7. Effect on brightness of some trivalent elements.

killer action of the element. On the basis of this, Al may still be considered as the best choice. Only the effect of Ce was sufficiently pronounced to be significant. Since these phosphors were not fired in a reducing atmosphere (12) it is possible that at least part of the Ce existed in tetravalent form.

*Miscellaneous impurities.*—The effect of several miscellaneous impurities tested is shown in Fig. 8. It can be seen that some elements are strong killers primarily at higher concentrations; Co and V, however, have an influence even at very low concentrations (10 ppm) which exceeds that of any other element tested. A slight enhancing effect was noted in the neighborhood of 100 ppm for Zr. Inasmuch as there is no apparent correlation between the observed killing action and other more general parameters of any of these elements, these particular results require no further comment. However, it should be stressed that any small effects (of the order of 1%) observed in this study are necessarily uncertain, and may have resulted from differences in particle size distribution as well as possibly other parameters caused by the particular impurity. Such influences might be eliminated during further processing of such phosphors in lamp making.

### Summary

The effect on plaque brightness of a number of impurity elements in a 3000°K calcium halophosphate phosphor has been investigated. Results for 100 ppm, 1000 ppm, and 1% impurity concentrations are summarized in Table I. Among those impurities which normally occur in S. L. grade raw materials in concentrations of 10-30 ppm, only Fe

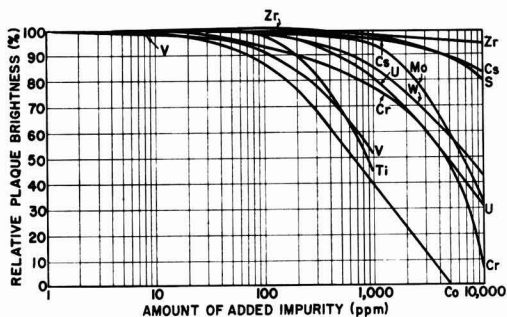


Fig. 8. Effect on brightness of some other less commonly occurring impurity elements.

Table I. Effect of impurity additions at 100 ppm, 1000 ppm, and 10,000 ppm on the plaque brightness of a 3000°K calcium halophosphate phosphor. All values are normalized to 100 for 1 ppm added impurity and arranged according to increasing killer effect.

100 ppm added		1000 ppm added		10,000 ppm added	
Impurity	Output	Impurity	Output	Impurity	Output
Ce	101.1	Al	100.5	Al	99.5
Al	100.9	Ce	98.8	Zr	95.2
Zr	100.9	Ag	88.8	Ce	93.2
Pb	100.8	S	97.8	La	92.5
Ga	100.8	Pb	97.7	Pb	91.7
La	100.6	Zr	97.6	Y	89.6
S	100.2	Si	97.5	In	89.2
Na	100.2	La	97.0	Sm	86.2
Si	100.1	In	96.9	Cs	83.5
Sm	99.8	Cs	96.7	S	79.7
Ag	99.7	Y	95.3	Pr	78.8
Cs	99.5	Sm	95.1	Nd	61.0
Mo	99.5	Mo	95.0	Na	48.5
Pr	99.5	Ga	94.8	Ag	46.7
Sn	98.9	Pr	92.5	Sn	45.8
Y	98.8	Nd	88.5	W	42.7
In	98.5	Na	88.5	Si	41.8
U	98.5	W	85.7	Mo	32.3
W	98.3	Sn	81.8	U	31.3
Nd	98.2	U	81.7	Ga	18.1
Ti	98.1	Cr	77.9	Cr	7.57
Cr	93.5	Fe	62.3	Ni	3.96
Cu	92.5	Ni	53.6	Fe	0.72
Ni	92.3	V	51.3	Cu	—
V	91.8	Cu	50.7	Co	—
Fe	91.7	Ti	44.9	V	—
Co	87.3	Co	39.6	Ti	—

is believed to exert a sufficient influence to affect the phosphor output appreciably. Enhancing effects of the order of 1% or slightly less were noted for Al, Ce, Ga, La, Zr, and Pb. The results of some preparatory work on purification procedures for raw materials, as well as a reproducible technique for firing, have also been described. It is believed that any reduction in fluorescent brightness observed would probably be reflected in zero-hour lamp readings. Because of this, the results obtained allow a reasonable selection of impurities and concentration ranges for lamp testing.

### Acknowledgments

The author is indebted to Miss I. Walinski and Mr. G. Scanlon for the purification of chemicals and the preparation and measurements of the phosphors, as well as to Mr. R. W. Wollentin who helped in the design of the plaque tester. Messrs. I. Meister and T. Ellis performed the spectrographic analyses, and Messrs W. Lilliendahl and E. Biter performed chemical analyses for iron to correlate with the spectrographic results. Helpful discussions with Professor E. Banks are gratefully acknowledged. Thanks are also due to Dr. H. F. Ivey for reading and suggesting improvements in the original manuscript.

Manuscript received Oct. 3, 1957. This paper was prepared for delivery before the New York Meeting, April 27-May 1, 1958.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1958 JOURNAL.

### REFERENCES

- H. G. Jenkins, A. H. McKeag, and P. W. Ranby, *This Journal*, **96**, 1 (1949).
- R. Nagy, R. W. Wollentin, and C. K. Lui, *ibid.*, **96**, 187 (1949).
- K. H. Butler, U. S. Pat. 2,755,254, July 17, 1956.
- K. H. Butler, M. J. Bergin, and V. M. B. Hannaford, *This Journal*, **97**, 117 (1950).
- R. Ward, R. K. Osterheld, and R. D. Rosenstein, "Inorganic Syntheses," L. F. Audrieth, Editor, Vol. III, p. 11, McGraw Hill Book Co., Inc., New York (1950).
- K. H. Butler and R. W. Mooney, *Sylvania Techn.*, **9**, #4, (October, 1956).
- Sylvania Electric Prod. Inc., Brit. Pat. 691,140, May 6, 1953.
- A. H. McKeag and P. W. Ranby, General Electric Co., Brit. Pat. 580,363, Sept. 5, 1946.
- J. L. Ouweltjes, *J. phys. radium*, **17**, 641 (1956).
- E. Banks, Polytechnic Institute of Brooklyn, Private communication.
- W. L. Wanmaker and M. G. A. Tak, *Electrochem. Soc. Enlarged Abstract #45*, Electronics Division, Washington Meeting (1957).
- S. T. Henderson and P. W. Ranby, *This Journal*, **104**, 612 (1957).

# Polarographic Reduction of Delta-3-Ketosteroids<sup>4</sup> in Well-Buffered Media

Peter Kabasakalian and James McGlotten

Research Division, Schering Corporation, Bloomfield, New Jersey

## ABSTRACT

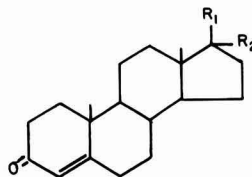
The polarographic reduction of progesterone, testosterone, methyltestosterone, testosterone propionate, 17-hydroxyprogesterone, 11-deoxycorticosterone, 11-deoxycorticosterone acetate, and 11-deoxy-17-hydroxycorticosterone has been studied in relation to the changes in the wave effected by pH, temperature, concentration, and mercury pressure. The system used was 50% aqueous alcohol with organic buffers. Testosterone was also examined at pH 7 and above in phosphate and borate buffers. Wave splitting was found in these buffers that was nonexistent at comparable pH values in organic buffers.

The need for adequate buffering in the polarographic reduction of many organic compounds has by now been firmly established. Just what constitutes a good polarographic buffer in the alcoholic solutions so often necessary in the polarography of organic compounds has not been clarified. The problem of buffer choice seems to be most troublesome in the basic regions.

The polarographic buffering ability (in water-alcohol solutions) of the phosphate and borate buffers often used to obtain a pH of 7 or higher is open to question in view of the results obtained with azobenzene (1) in these buffers. Quite different results have been obtained for this compound by other workers (2,3) using different buffer components. Zuman, *et al.* (4), have published some work on the polarographic reduction of  $\Delta^3$ -ketosteroids in water-ethanol solutions buffered with Britton and Robinson buffers (acetic, phosphoric, and boric acids). These authors reported that the steroids investigated gave two waves in basic solutions. The relative heights of these two waves varied as the pH of the solutions was varied, with the total height remaining relatively constant. The presence of these two waves was attributed to forms interconvertible with pH. Recently Lund (5) has reported the polarographic behavior of progesterone and androsta-1, 4-diene-17 $\beta$ -ol-3-one in 75% methanol-25% water solutions containing 0.5M LiCl and 0.05M buffer. He reported having obtained only one wave for these compounds over the basic region.

This work presents, primarily, the polarographic behavior of eight steroids [progesterone (I), testosterone (II), methyltestosterone (III), testosterone propionate (IV), 17-hydroxyprogesterone (V), 11-deoxycorticosterone (VI), 11-deoxycorticosterone acetate (VII), 11-deoxy-17-hydroxycorticosterone (VIII)] in what is believed to be adequately buffered 50% ethanol solutions containing organic buffering materials which cover the pH range from pH 1.3 to 10.5 without any large gap between pH

values such as was present in an earlier paper (6). Some work with testosterone in phosphate and borate buffers is also presented.



COMPOUND	R <sub>1</sub>	R <sub>2</sub>
I	-COCH <sub>3</sub>	--H
II	--OH	--H
III	--OH	-CH <sub>3</sub>
IV	--OCOC <sub>2</sub> H <sub>5</sub>	-H
V	-COCH <sub>3</sub>	--OH
VI	-COCH <sub>2</sub> OH	--H
VII	-COCH <sub>2</sub> OCOCH <sub>3</sub>	--H
VIII	-COCH <sub>2</sub> OH	--OH

## Experimental

**Apparatus and materials.**—All of the experimental work was performed on the Sargent Model XXI recording polarograph. The cells used for most of the work were small H-type cells (3-ml sample volume) containing a normal calomel electrode separated from the sample compartment by an agar plug and fritted glass diaphragm. However, 10 ml cells employing a mercury pool anode were used in the diffusion current vs. temperature studies. These cells permitted a small Anschutz precision thermometer to be immersed directly in the sample solution along with the capillary.

The electrode capillary delivered 1.768 mg of Hg/sec at a column height of 44.5 cm. The drop time was 4.01 sec and the capillary constant,  $m^{2/3}t^{1/6}$ , was 1.842 mg<sup>2/3</sup> sec<sup>-1/2</sup>. The constants were determined

at an open circuit with the mercury dropping into a 0.1N potassium chloride solution.

The apparatus used in the diffusion coefficient experiments was essentially that of Stokes (7).

The absolute ethanol and buffer components were found to be polarographically inert in the desired voltage range. The steroids used in this investigation were obtained from the Schering Laboratories. The Triton X-100 was obtained from Rohm and Haas.

**Procedure.**—Electrolysis solutions for all of the qualitative work were prepared by pipetting 5 ml aliquots of an alcoholic steroidal solution into a 10 ml volumetric flask, adding 0.1 ml of 0.2% Triton X-100 and diluting to the mark with the appropriate aqueous buffer solution. Portions of the electrolysis solution were used to rinse the sample cell, a final portion was deaerated with nitrogen for 10 min and then electrolyzed. The pH of the solutions was determined after electrolysis. For the current-concentration work the sample was weighed directly into the 10 ml volumetric flask using a micro balance and dissolved in 5 ml of alcohol. Diffusion currents were determined by the method of intersecting lines. The buffer system used for the major part of this work is presented in Table I.

### Results and Discussion

**Effect of pH on half-wave potentials.**—The half-wave potentials of each steroid investigated decreased linearly with an increase in pH throughout the pH range from 1.3 to 10.5. The slopes of the  $E_{1/2}$  vs. pH plots varied between 0.059 and 0.063 v/pH unit with a mean value of 0.060 v/pH unit. There were no deviations from this pH dependency observed for methyltestosterone, testosterone, or progesterone as had been observed in Britton and Robinson buffers. A comparison of the testosterone  $E_{1/2}$  vs. pH plot obtained by Zuman, *et al.* (4), and that obtained in this investigation is presented in Fig. 1. The experimental data for all the steroids are compiled in Table II. The data presented by Lund (5) for progesterone show that the half-wave potentials at the basic pH values (9.80, 10.16, and 11.0) are more negative than would be expected from the slope of the line determined by the half-waves at

Table I. Composition of buffers\* in 50% ethanol

pH	Buffer components		
1.3	0.100 M	HCl	
3.0	0.100 M	malonic acid	+0.025M KOH
4.0	0.100 M	malonic acid	+0.075M KOH
5.2	0.075 M	acetic acid	+0.025M NaOAc
5.7	0.050 M	acetic acid	+0.050M NaOAc
6.2	0.025 M	acetic acid	+0.075M NaOAc
6.9	0.100 M	malonic acid	+0.170M KOH
8.6	0.100 M	trimethylamine	+0.075M HCl
9.1	0.100 M	trimethylamine	+0.050M HCl
9.5	0.100 M	triethylamine	+0.075M HCl
10.0	0.100 M	triethylamine	+0.050M HCl
10.5	0.100 M	triethylamine	+0.025M HCl

\* Potassium chloride was added as an ionic strength agent.

the acidic pH values (1.05, 4.00, and 5.08). In an attempt to extend the  $E_{1/2}$  vs. pH data for borate buffers, testosterone was examined in borate buffers at pH 7.7, 8.5, 10.0, and 11.1 as well as a citric acid-disodium phosphate buffer pH 4.7 for comparison. The  $E_{1/2}$  vs. pH relationship was complicated by the fact that wave splitting similar to that described by Zuman (4) occurred in the solutions of pH 7.7 and 8.5. However, the one wave obtained at pH 4.7 and the small first waves obtained at pH 7.7 and 8.5

Table II. Effect of pH on half-wave potential and diffusion current

pH	Progesterone		Testosterone		Methyltestosterone		Testosterone propionate	
	$-E_{1/2}^*$	$k^{**}$	$-E_{1/2}$	$k$	$-E_{1/2}$	$k$	$-E_{1/2}$	$k$
1.3	1.11	2.01	1.13	1.76	1.13	1.78	1.13	1.93
3.0	1.21	1.92	1.23	1.74	1.23	1.71	1.23	1.91
4.0	1.27	1.82	1.29	1.76	1.30	1.61	1.29	1.78
5.2	1.35	1.81	1.37	1.63	1.37	1.62	1.36	1.74
5.7	1.38	1.77	1.40	1.78	1.41	1.53	1.39	1.68
6.2	1.41	1.70	1.43	1.69	1.44	1.56	1.43	1.72
6.9	1.46	1.73	1.47	1.68	1.47	1.43	1.46	1.63
8.6	1.57	1.82	1.57	1.53	1.57	1.58	1.57	1.52
9.1	1.59	1.74	1.60	1.62	1.60	1.42	1.60	1.52
9.5	1.62	1.60	1.63	1.49	1.62	1.46	1.62	1.46
10.0	1.65	1.68	1.66	1.50	1.65	1.46	1.65	1.40
10.5	1.68	1.70	1.69	1.46	1.68	1.48	1.68	1.47
Slope†	= 0.063		0.061		0.059		0.060	

pH	17-Hydroxyprogesterone		11-Deoxycorticosterone		11-Deoxycorticosterone acetate		11-Deoxy-17-hydroxycorticosterone	
	$-E_{1/2}$	$k$	$-E_{1/2}$	$k$	$-E_{1/2}$	$k$	$-E_{1/2}$	$k$
1.3	1.14	2.09	1.12	2.31	1.11	1.92	1.15	2.10
3.0	1.24	2.02	1.22	1.80	1.21	2.06	1.24	1.74
4.0	1.31	1.90	1.29	1.58	1.28	1.64	1.31	1.76
5.2	1.37	1.78	1.36	1.57	1.35	1.43	1.38	1.71
5.7	1.40	1.72	1.39	1.58	1.38	1.43	1.41	1.68
6.2	1.44	1.70	1.42	1.58	1.43	1.43	1.45	1.63
6.9	1.48	1.53	1.46	1.65	1.46	1.61	1.49	1.54
8.6	1.57	1.62	1.57	1.83	1.55	1.84	1.58	1.60
9.1	1.60	1.61	1.60	1.86	1.58	1.76	1.60	1.62
9.5	1.62	1.54	1.62	1.66	1.62	1.54	1.63	1.36
10.0	1.65	1.61	1.64	1.50	1.64	1.47	1.66	1.41
10.5	1.68	1.57	1.67	1.51	1.67	1.45	1.69	1.36
Slope	= 0.059		0.059		0.060		0.059	

\* Half-wave potentials in volts measured against a normal calomel electrode.

\*\*  $k$  = microamperes per millimolar.

† Slope at 25°C in v/pH units.

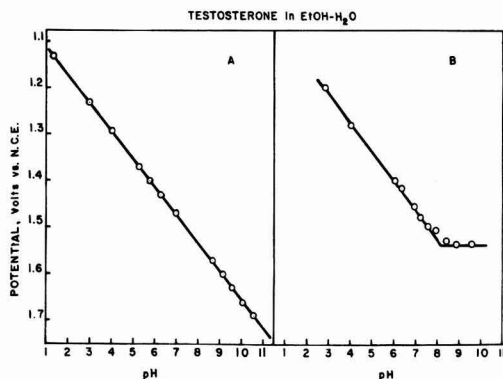


Fig. 1. Variation of  $E_{1/2}$  with pH for testosterone using (A) buffers used in this study and (B) buffers used by Zuman and co-workers.



Table III. Testosterone in 75% CH<sub>3</sub>OH

pH	Buffer composition	$-E_{1/2}$ $\nu$	$-E_{1/2}$ $\nu$
4.7	0.050M citric acid	1.29	—
	0.060M disodium phosphate		
7.7	0.075M hydrochloric acid	1.45	1.63
	0.050M sodium tetraborate		
8.5	0.045M hydrochloric acid	1.50	1.63
	0.050M sodium tetraborate		
10.0	0.068M sodium hydroxide	—	1.66
	0.050M sodium tetraborate		
11.1	0.100M sodium hydroxide	—	1.72
	0.050M sodium tetraborate		
0.5M LiCl added			

fall on a straight line whose slope is approximately 0.059  $\nu$ /pH unit. The  $E_{1/2}$  of the second and main wave at pH 7.7 and 8.5 was invariant at both pH values. This wave began to shift to more negative potentials at pH 10.0 and 11.1. The data are listed in Table III.

*Effect of pH on diffusion current.*—The diffusion currents obtained with eight steroids were substantially pH independent. However, the currents obtained in acid solutions were slightly larger than those obtained in basic solutions for all of the steroids examined with the exception of deoxycorticosterone and deoxycorticosterone acetate. The diffusion current constants obtained at the various pH values are listed in Table II.

*Effect of concentration on diffusion current.*—The diffusion currents obtained with progesterone, testosterone, methyltestosterone, 11-deoxy-17-hydroxycorticosterone, and testosterone propionate were found to be directly dependent upon concentration from approximately  $2 \times 10^{-4}M$  to  $1 \times 10^{-2}M$ . With deoxycorticosterone and deoxycorticosterone acetate the current-concentration relationship appears to deviate from linearity at the lower end of this concentration range. However, the diffusion plateau for those two compounds at this point was so steep that the deviation may be due more to the method of measurement than to any change in diffusion properties.

*Effect of temperature on diffusion current.*—The variation of diffusion current with temperature was determined for the eight steroids over a temperature range from 7° to 50°C. The temperature coefficients for these  $\Delta^4$ -3-ketosteroids averaged  $1.94 \pm 0.08\%$  per degree with respect to the 25°C value. The coefficients are in keeping with diffusion-controlled processes.

*Effect of mercury height on diffusion currents.*—The effect of mercury pressure on the diffusion currents obtained with these steroids was studied in 50% ethanol solutions buffered at pH 5.5 with acetic acid-sodium acetate buffer. The ratios of the currents obtained at two different mercury heights averaged  $1.34 \pm 0.01$ . Ratios of 1.00, 1.38, and 1.92 would be expected for kinetic, diffusion, and adsorption control, respectively, for the two mercury heights employed.

*Determination of diffusion coefficients by the diaphragm cell technique.*—Diffusion coefficients of

2.37, 2.31, 2.53, 2.25, 2.22, 2.54, 2.33, and 2.07 (in units of  $10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup>) were obtained for progesterone, testosterone, methyltestosterone, testosterone propionate, 17-hydroxyprogesterone, 11-deoxycorticosterone, 11-deoxycorticosterone acetate, 11-deoxy-17-hydroxycorticosterone, respectively. On substitution in the modified Ilkovic equation (8) these diffusion coefficients yield  $n$  values of 1.04, 1.02, 0.93, 1.01, 1.06, 0.90, 0.83, and 1.02 for the reduction of the steroids as listed above. This indicates that the reduction mechanism is the same as that reported earlier (6), i.e., bimolecular reduction to a pinacol.

*Wave form.*—Essentially the reduction of each of the steroid compounds is characterized by a single, regular S shaped curve. Three compounds exhibit an additional wave at pHs 3.0 and 4.0. This wave, apparently catalytic in nature, is observed with progesterone, 11-deoxycorticosterone, and 11-deoxycorticosterone acetate. It is interesting to note that this wave is not observed with 17-hydroxyprogesterone or 11-deoxy-17-hydroxycorticosterone. The addition of the 17-hydroxy group seems to have an inhibitory effect on this catalytic wave.

There was no double wave observed for any of these compounds in basic media contrary to previous reports. Zuman, *et al.* (4), observed two waves with testosterone, methyltestosterone, progesterone, and deoxycorticosterone in ethanol-water systems buffered with Britton and Robinson buffers. The heights of the two waves were found to vary with pH, the total height remaining relatively constant. The pH interval over which two waves were obtained varied for the different steroids; however, no wave splitting was found below pH 5 or above pH 11 for any of the compounds. Since no wave splitting was evidenced by the four steroids listed above anywhere in this pH range in the organic buffers used here, it would appear that the double waves observed by Zuman and his co-workers were due to the buffers used rather than the pH of the solution as had been postulated.

If equation (I)



where S = unsaturated ketosteroid and SH<sup>+</sup> = steroid-hydrogen ion complex, represented a reaction between a steroid and a *specific buffer acid* (rather than a generalized acid-base reaction) then an equilibrium constant could be written

$$K = \frac{[SH^+][HPO_4^{2-}]}{[S][H_2PO_4^-]}$$

which, with appropriate K and HPO<sub>4</sub><sup>2-</sup>/H<sub>2</sub>PO<sub>4</sub><sup>-</sup> values, could account for two waves observed in buffer solutions which contain excess acid component providing the equilibrium at the electrode surface is re-established slowly. The fact that the first wave increases directly with steroid concentration, decreases with increasing salt (HPO<sub>4</sub><sup>2-</sup>) concentration at constant acid concentration, and remains relatively constant upon increasing buffer concentration while maintaining HPO<sub>4</sub><sup>2-</sup>/H<sub>2</sub>PO<sub>4</sub><sup>-</sup> constant would be understandable if such an equilibrium existed for phos-

Table IV. Effect of steroid concentration, buffer concentration, and salt to acid ratio on the two waves in phosphate buffered solutions. 50% Ethanol solutions of testosterone

Steroid conc	Buffer conc	<i>i</i> (obs)	<i>i</i> (theory)
(a) Varying steroid conc			
0.33mM	0.030 M $\text{KH}_2\text{PO}_4$ + 0.045 M $\text{K}_2\text{HPO}_4$	0.31 $\mu\text{A}$	0.55 $\mu\text{A}$
0.65mM	0.030 M $\text{KH}_2\text{PO}_4$ + 0.045 M $\text{K}_2\text{HPO}_4$	0.61 $\mu\text{A}$	1.01 $\mu\text{A}$
1.62mM	0.030 M $\text{KH}_2\text{PO}_4$ + 0.045 M $\text{K}_2\text{HPO}_4$	1.47 $\mu\text{A}$	2.69 $\mu\text{A}$
3.25mM	0.030 M $\text{KH}_2\text{PO}_4$ + 0.045 M $\text{K}_2\text{HPO}_4$	2.86 $\mu\text{A}$	5.40 $\mu\text{A}$
(b) Varying salt to acid ratio			
1.0mM	0.025 M $\text{KH}_2\text{PO}_4$ + 0.050 M $\text{K}_2\text{HPO}_4$	0.83 $\mu\text{A}$	1.66 $\mu\text{A}$
1.0mM	0.050 M $\text{KH}_2\text{PO}_4$ + 0.050 M $\text{K}_2\text{HPO}_4$	1.12 $\mu\text{A}$	1.66 $\mu\text{A}$
1.0mM	0.075 M $\text{KH}_2\text{PO}_4$ + 0.050 M $\text{K}_2\text{HPO}_4$	1.25 $\mu\text{A}$	1.66 $\mu\text{A}$
1.0mM	0.075 M $\text{KH}_2\text{PO}_4$ + 0.025 M $\text{K}_2\text{HPO}_4$	1.44 $\mu\text{A}$	1.66 $\mu\text{A}$
(c) Varying buffer conc			
1.0mM	0.006 M $\text{KH}_2\text{PO}_4$ + 0.004 M $\text{K}_2\text{HPO}_4$	1.04 $\mu\text{A}$	1.66 $\mu\text{A}$
1.0mM	0.015 M $\text{KH}_2\text{PO}_4$ + 0.010 M $\text{K}_2\text{HPO}_4$	1.16 $\mu\text{A}$	1.66 $\mu\text{A}$
1.0mM	0.030 M $\text{KH}_2\text{PO}_4$ + 0.020 M $\text{K}_2\text{HPO}_4$	1.25 $\mu\text{A}$	1.66 $\mu\text{A}$
1.0mM	0.060 M $\text{KH}_2\text{PO}_4$ + 0.040 M $\text{K}_2\text{HPO}_4$	1.27 $\mu\text{A}$	1.66 $\mu\text{A}$

*i* (obs) = current observed for the pH controlled first wave; *i* (theory) = current obtained for same wave in well-buffered solutions.

Table V. Determination of the equilibrium constant for the proposed steroid-hydrogen ion complex in phosphate and borate buffers. 50% Ethanol solutions of 1.0mM testosterone

Buffer Composition	<i>i</i> / <i>i'</i>	K
0.025 M $\text{KH}_2\text{PO}_4$ + 0.050 M $\text{K}_2\text{HPO}_4$	1.0	2.0
0.050 M $\text{KH}_2\text{PO}_4$ + 0.050 M $\text{K}_2\text{HPO}_4$	2.1	2.1
0.075 M $\text{KH}_2\text{PO}_4$ + 0.050 M $\text{K}_2\text{HPO}_4$	3.0	2.0
0.075 M $\text{KH}_2\text{PO}_4$ + 0.025 M $\text{K}_2\text{HPO}_4$	6.5	2.2
0.208 M $\text{H}_3\text{BO}_3$ + 0.012 M $\text{NaH}_2\text{BO}_3$	0.2	0.013
0.212 M $\text{H}_3\text{BO}_3$ + 0.008 M $\text{NaH}_2\text{BO}_3$	0.4	0.015
0.214 M $\text{H}_3\text{BO}_3$ + 0.006 M $\text{NaH}_2\text{BO}_3$	0.5	0.014
0.216 M $\text{H}_3\text{BO}_3$ + 0.004 M $\text{NaH}_2\text{BO}_3$	0.9	0.018
0.2 M KCl added		

*i* = current observed for pH controlled first wave; *i'* = current observed for pH independent second wave.

phate solutions (see Table IV). The slight increase in current occasioned by the increase in buffer constituents is not nearly as great as would be predicted by the equation developed by Koutecky (9) for the average current of an electrode reaction governed by the rate of diffusion of reactants and by the rate of dissociation of the buffer. Similar results were obtained with borate buffers. Table V shows values of K calculated for a series of phosphate and borate buffers.

In summary it can be said that the double wave obtained in the one electron reduction of  $\Delta^4$ -3-ketosteroids in 50% ethanol solutions buffered with phosphate or borate buffers (and combinations of the two) is not due to the pH of the solution, but to the buffer components. It has been shown that this wave splitting can be avoided by using tertiary amines as the buffer constituents for the higher pH range, rather than the inorganic phosphates and borates.

Manuscript received July 5, 1957. This paper was prepared 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 1958 JOURNAL.

## REFERENCES

1. A. Foffani and M. Fragiaco, *Ricerca sci.*, **22**, 139 (1955).
2. C. R. Castor and J. H. Saylor, *J. Am. Chem. Soc.*, **75**, 1427 (1953).
3. S. Wawzonek and J. D. Fredrickson, *ibid.*, **77**, 3985 (1955).
4. P. Zuman, J. Tenygl, and M. Brezina, *Collection Czechoslov. Chem. Commun.*, **19**, 46 (1954).
5. H. Lund, *Acta Chem. Scand.*, **11**, 283 (1957).
6. P. Kabasakalian and J. McGlotten, *J. Am. Chem. Soc.*, **78**, 5032 (1956).
7. R. H. Stokes, *ibid.*, **72**, 763 (1950).
8. J. J. Lingane and B. A. Loveridge, *ibid.*, **72**, 438 (1950).
9. J. Koutecky, *Collection Czechoslov. Chem. Commun.*, **19**, 857 (1954).



short side tubes near the bottom. The anolyte and catholyte were prevented from mixing by a filter paper plug in the side tube of the anode compartment, and the two halves of the cell were connected by a short length of rubber tubing. The compartments were closed by rubber bungs which carried the cell components. The anode, from which the discharge occurred, was of platinum wire connected to a tungsten rod sealed into a glass holder; the cathode was a small sheet of platinum foil. The anode and cathode compartments were connected separately to the vacuum line through small ground glass joints which permitted easy removal of the cell. The anolyte was stirred during electrolysis by a magnetic stirrer. To remove the considerable heat dissipated in the discharge, the cell was almost completely immersed in a bath through which a rapid stream of tap water was passed.

The vacuum system was of a conventional type but included a float manostat so that the pressure in the apparatus could be kept constant over long periods. Before each electrolysis the cell was evacuated to the vapor pressure of the solution. It was then filled with the gaseous atmosphere to be used (usually hydrogen) at atmospheric pressure and the system pumped down to the pressure to be used in the experiment; during electrolysis a slow stream of the gas was admitted to the anode compartment. Current was supplied from a Leland rectifier unit of adjustable voltage (0-1500 v) through a calibrated milliammeter and suitable ballast resistance (2000-10,000 ohms). The discharge was initiated by a pulse from an induction coil; once started it required about 600 v and the current could be kept steady at any desired value between 25 and 100 ma. The standard conditions of electrolysis were to use a current of 75 ma in an atmosphere of hydrogen at a pressure of 50 mm, the anode being 0.75 cm from the surface of 50 ml of anolyte, and the average temperature about 23°C.

The medium used for electrolysis has usually been either 0.8*N*-sulfuric acid (for ferrous and cerous sulfate experiments), or a phosphate buffer (0.1*M*- $\text{KH}_2\text{PO}_4$  + 0.1*M*- $\text{Na}_2\text{HPO}_4$ ) where a neutral medium was desirable (for ferrocyanide and azide experiments). The anolyte was made from a weighed quantity of the substrate dissolved in the medium; the catholyte was the medium alone. Analytical grade reagents were used throughout. Standard volumetric methods could be employed in most cases for the analysis of the solutions. Ferrous ion was estimated by titration with permanganate; azide was found by oxidation with excess ceric sulfate followed by addition of potassium iodide and back titration with thiosulfate; ceric ion was assessed by reduction with excess ferrous sulfate and back titration with ceric sulfate; hydrogen peroxide when formed was usually determined colorimetrically with titanous sulfate. The analysis of mixtures containing ferro and ferricyanides and hydrogen peroxide presented a difficult problem. It was solved by estimating hydrogen peroxide + ferrocyanide by oxidation with ceric sulfate, while ferricyanide + hydrogen peroxide were found iodometrically; fi-

nally, by combination of the two procedures, total ferro + ferricyanide could be obtained.

The substrates had been chosen to give simple oxidation reactions and this was found generally to be the case, although some slight disintegration of ferricyanide occurred on prolonged glow-discharge electrolysis; small quantities of ammonia accompanied the nitrogen which was the main oxidation product from azide. In all cases by complete analysis of both gaseous products and those in solution a satisfactory weight and oxidation/reduction balance was established.

### Characteristics of the Discharge

The discharge took the form of a sharply defined cone between the tip of the anode and the electrolyte surface. By photographing it under different conditions of current, pressure, electrode distance, etc., it was possible to determine the variation of current density at the surface with the above factors. Variation of current produced no significant change, the spot area increasing linearly with increase of current. With decrease of pressure, current density decreased and the relation  $I p^{-1} = 0.03$  held over the pressure range 3-10 cm of mercury, where  $I$  was the current density in amp/cm<sup>2</sup> and  $p$  the pressure in cm of mercury. Current density was found to vary inversely with electrode distance from the surface, but the effect was relatively slight.

To determine the fall of potential near the liquid surface a probe of platinum wire was inserted in the discharge and the voltage between it and the cathode measured on a valve voltmeter. Under the conditions of operation it was expected that the fall would occur very close to the surface of the solution, certainly within 1 mm. In practice it was not possible to have the probe nearer to the surface than this and a process of extrapolation was applied to determine the cathode fall. The probe voltage was measured at various probe-surface distances at various pressures. The results are shown in Fig. 2 whence it can be seen that the cathode fall is 415 v and occurs at a distance of less than 0.05 cm from the surface of the solution. This value was unaffected by the gaseous atmosphere, by the pressure, by the current, by the electrode-surface distance, or by the nature of the electrolyte.

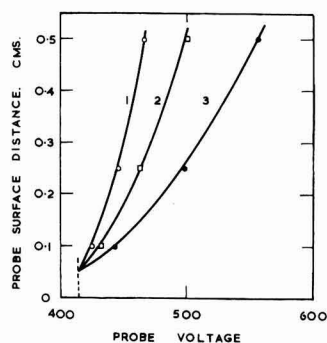


Fig. 2. Determination of potential drop near liquid surface: pressures (1) 27, (2) 50, and (3) 100 mm mercury.

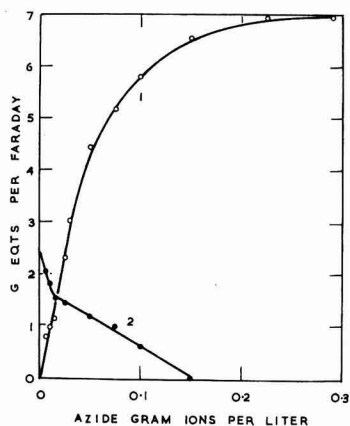


Fig. 3a. Variation of yield with concentration of substrate: curve 1, substrate oxidized; curve 2, hydrogen peroxide formed.

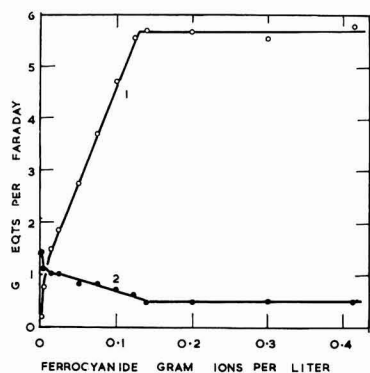


Fig. 3b. Variation of yield with concentration of substrate: curve 1, substrate oxidized; curve 2, hydrogen peroxide formed.

The glow was examined using a Hilger Medium Quartz Spectrograph but, apart from showing the presence of the OH radical and diffuse absorption bands in the near ultraviolet probably due to some polyatomic hydrogen-oxygen species, the spectrograms furnished little specific information on the discharge.

### Results

Experimental variables fall into two categories. Of prime importance are the quantity of electricity passed, the concentration of the substrate, the pressure of the gas in the cell, and in some cases the presence of chloride ion in solution. Factors such as current, electrode distance, and the nature of the gas in the cell, although they may affect the power dissipated in the discharge considerably, usually have only a trivial influence on the yield of chemical products. The most useful way of summarizing the results of glow-discharge electrolysis is by quoting the instantaneous or differential yield of the product at the initial concentration of substrate. This quantity is denoted in this paper by  $G$  and is given in equivalent/faraday; it is analogous in some ways to the quantity used in radiation chemistry where the yield is expressed in molecules/100 ev.

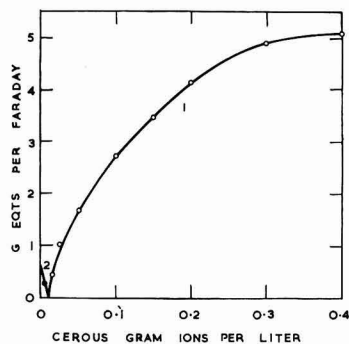


Fig. 3c. Variation of yield with concentration of substrate: curve 1, substrate oxidized; curve 2, hydrogen peroxide formed.

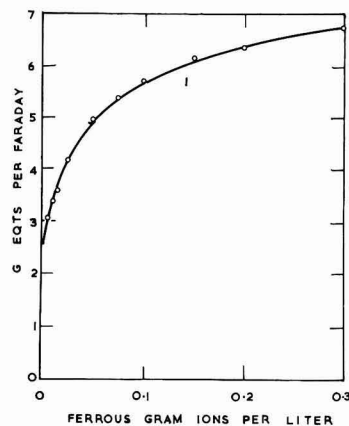


Fig. 3d. Variation of yield with concentration of substrate: curve 1, substrate oxidized.

Values of  $G$  in the present work have been obtained from experimental curves of yield plotted against quantity of electricity passed under different experimental conditions; the slope of the tangent to such a curve at the origin gives the corresponding  $G$  value. The general results obtained in the glow-discharge electrolysis of sodium azide, cerous sulfate, and potassium ferrocyanide are compared below, together with those obtained using ferrous sulfate in an earlier study (4).

*Influence of concentration.*—In Fig. 3a-d are shown graphs of the differential yield of oxidation product plotted against the concentration of substrate in the four cases; where hydrogen peroxide was formed the yield of this is also indicated (Curve 2).

In general it is seen that the differential yield increases with increasing concentration of substrate and approaches a limiting value asymptotically; the ferrocyanide case is abnormal here in that, over a substantial range of concentrations, the yield is accurately proportional to the concentration, and the limiting value is attained abruptly when the concentration is 0.125M. The behavior at low concentrations depends on the reaction of the substrate or its oxidation product with hydrogen peroxide. Where the substrate is readily oxidized by hydro-



gen peroxide, as is the case with ferrous sulfate, there is a finite oxidation yield even at zero concentration. On the other hand, where the oxidation product can be reduced by hydrogen peroxide, e.g., ceric sulfate, a certain minimum concentration of substrate is necessary for any oxidation to occur. Where hydrogen peroxide cannot react in either way, its formation accompanies the oxidation of the substrate, the hydrogen peroxide yield diminishing with increasing substrate concentration. This is seen in the azide and ferrocyanide examples, although it is noteworthy that even at the highest ferrocyanide concentrations there is still a small yield of hydrogen peroxide.

*Effect of pressure.*—With rise of pressure, i.e., increase of current density in the glow-spot, oxidation yields were found in general to fall. This is illustrated by the following figures which refer to a concentration of substrate of 0.025M in each case.

Pressure mm	Fe <sup>2+</sup>	G equivalents/faraday N <sub>2</sub>	Fe(CN) <sub>6</sub> <sup>4-</sup>	Ce <sup>2+</sup>
30	4.3	2.7	2.4	1.5
50	4.2	2.3	1.9	1.0
75	4.2	1.8	1.6	0.6

The effect seems most marked where the oxidation yield is low, and is relatively slight in the ferrous case.

*Influence of chloride.*—In the glow-discharge electrolysis of inert electrolytes the presence of chloride ion at concentrations greater than 0.02M seems to inhibit the formation of hydrogen peroxide, although it is not appreciably consumed, and its effect has therefore been tested in the present oxidation studies. With ferrous sulfate, sodium azide and cerous sulfate the presence of 0.02M-sodium chloride in the electrolyte decreased the oxidation yields appreciably, but with potassium ferrocyanide the oxidation yield of ferricyanide was scarcely affected, although that of the accompanying hydrogen peroxide was reduced.

*Miscellaneous factors.*—Variation of temperature is possible over a limited range of about 20°–40°C. The oxidation yield has usually been found to increase somewhat with rise of temperature, but this is not invariably so and, in the case of azide, an appreciable decrease was noted. Working with oxygen-saturated solutions of ferrous sulfate and with an oxygen atmosphere in the cell, the limiting G value at high concentrations was notably increased from about 7.0 to 12.5 equivalents/faraday; with all the other substrates investigated, however, the presence of oxygen had little effect. In the investigation of the formation of hydrogen peroxide in inert electrolytes (3) a salt effect was noted whereby the yield was increased by raising electrolyte concentration. In the present work it has been found that where the substrate is oxidized by hydrogen peroxide, as in the ferrous case, a similar rise in oxidation yield occurs, but where the substrate is fairly stable to hydrogen peroxide, as in the ferrocyanide and azide cases, little salt effect is apparent, and with cerous sulfate where the oxidation product is reduced by hydrogen peroxide the addition of sodium sulfate to the medium decreased the oxidation yield.

## Discussion

Since it seems improbable that electrons can be emitted directly from the surface of a liquid electrolyte, it follows that in experiments with a glow-discharge anode the current must be conveyed by positive gaseous ions which are driven into the liquid from the gas phase and subsequently discharged. The fact that the nature of the gas present has usually little influence on the process suggests that the discharge may well pass ultimately through water vapor in all cases and this is not unlikely since the local temperature under the glow spot must be relatively high. We have no certain knowledge of the nature of the ions present in ionized water vapor at pressures corresponding to those used in the present work, but observations made with the mass spectrometer at much lower pressures (5) have shown that the main positive ion present is H<sub>3</sub>O<sup>+</sup>, and for simplicity this will be assumed to be the species carrying the charge across the interface in the present experiments. Now, as previously mentioned, the main drop of potential is some 415 v and occurs in the discharge within about 0.05 cm of the liquid surface, and hence the maximum energy which the ions could have on entering the solution would be 415 ev. In practice, of course, much of this energy will be dissipated in collisions in the vapor phase and the average energy will depend on the mean free path of the ions in the discharge which cannot be calculated with any accuracy. Thus the particles are likely to have energies less than 415 ev and, while these are minute compared to those of most ionizing radiations, they may well be adequate to bring about dissociation of water molecules.

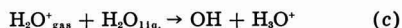
Thus in the primary reaction zone in the glow spot interaction of the gaseous ions with solvent molecules might be expected to produce dissociation by collision



or possibly



and to produce also 1 equivalent of OH per faraday by charge transference



Within this primary zone, interaction of the radicals among themselves is likely to be governed very largely by spatial considerations and is not amenable to treatment by conventional kinetics (6). However, once the active species have diffused out it should be possible to consider their reactions by ordinary kinetic methods. The OH radical may be expected to oxidize any suitable substrate S by the general reaction



In an inert electrolyte hydrogen peroxide is always formed, and this may be represented by the dimerisation



In addition there will be a back reaction which may be represented



Thus oxidation by glow-discharge electrolysis on this scheme will be determined by the competition of reactions (d), (e), and (f). Thus if  $n$  equivalents of OH are formed per faraday by the primary reactions (a), (b), and (c), and if  $v_1$ ,  $v_2$ , and  $v_3$  are the velocities of reactions (d), (e), and (f) in the stationary state, then the oxidation yield in equivalents per faraday will be given by

$$G(1) = n \cdot (v_1 + v_2) / (v_1 + v_2 + v_3) \quad (\text{I})$$

where the substrate is completely oxidized by hydrogen peroxide.

$$G(2) = n \cdot v_1 / (v_1 + v_2 + v_3) \quad (\text{II})$$

where the substrate and product are inert toward hydrogen peroxide.

$$G(3) = n \cdot (v_1 - v_2) / (v_1 + v_2 + v_3) \quad (\text{III})$$

where the oxidized product is completely reduced by hydrogen peroxide. If now the velocities are expressed in terms of the concentrations of the reacting species and rate constants  $k_1$ ,  $k_2$ , and  $k_3$  the corresponding relations are

$$G(1) = n \cdot ([S] + A) / ([S] + A + B) \quad (\text{IV})$$

$$G(2) = n \cdot [S] / ([S] + A + B) \quad (\text{V})$$

$$G(3) = n \cdot ([S] - A) / ([S] + A + B) \quad (\text{VI})$$

where  $A = k_2[\text{OH}]/k_1$  and  $B = k_3[\text{H}]/k_1$ .  $A$  and  $B$  would only be expected to be constant for a particular substrate in a particular set of conditions, but  $B/A = k_3[\text{H}]/k_2[\text{OH}]$  might be hoped to have some general significance if the stationary OH concentration does not vary widely with different substrates;  $n$  should, of course, be constant throughout. Ferrous sulfate, sodium azide, and cerous sulfate approximate to these three limiting cases (although sodium azide in concentrated solutions is slowly oxidized by hydrogen peroxide) and it is interesting to see how the experimental data fit the above relations. On taking reciprocals of the above expressions they become

$$\frac{1}{G(1)} = \frac{1}{n} \cdot \frac{B}{[S] + A} + \frac{1}{n} \quad (\text{VII})$$

$$\frac{1}{G(2)} = \frac{1}{n} \cdot \frac{A + B}{[S]} + \frac{1}{n} \quad (\text{VIII})$$

$$\frac{1}{G(3)} = \frac{1}{n} \cdot \frac{2A + B}{[S] - A} + \frac{1}{n} \quad (\text{IX})$$

Hence the plot of  $1/G$  against  $1/[S]$  should be a straight line in each case at high concentrations of substrate and the intercept on the  $1/G$  axis should be the same. In Fig. 4 the graphs are plotted; it is seen that they are linear at concentrations greater than 0.05N and converge to approximately a common point. From the slopes, values of  $B/n$ ,  $(A+B)/n$ , and  $(2A+B)/n$  can be obtained in the respective cases. To analyze these further, supplementary data are required and these are provided by the extrapolated behavior at very low substrate concentrations. In each case, the yield of hydrogen

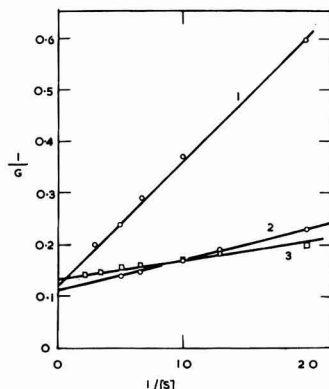


Fig. 4. Graphs of reciprocal yields against reciprocal concentrations of substrate: curve 1,  $\text{Ce}_2(\text{SO}_4)_3$ ; curve 2,  $\text{NaN}_3$ ; curve 3,  $\text{FeSO}_4$ .

peroxide in this limit should be  $n \cdot A / (A + B)$ ; in the ferrous sulfate case this will of course correspond to the limiting oxidation at zero substrate concentration (2.5 equivalent/faraday), while in the azide and cerous cases it will be the actual yields of hydrogen peroxide obtained, i.e., approximately 2.3 and 0.6 equivalent/faraday. Utilizing these data, the values of  $n$ ,  $A$ ,  $B$ , and  $B/A$  in the three cases have been evaluated and are summarized below; values of  $n$  are obtained from the intercepts on the  $1/G$  axis in Fig. 4, and the values of  $A$  and  $B$  are obtained from the slopes of the graphs combined with the yields at zero substrate concentration.

Substrate	$n$	$A$	$B$	$B/A$
$\text{FeSO}_4$	7.3	0.011	0.026	2.4
$\text{NaN}_3$	8.3	0.012	0.032	2.7
$\text{Ce}_2(\text{SO}_4)_3$	7.6	0.013	0.152	11.7

The values of  $n$  are approximately constant and  $B/A$  is of the same order of magnitude in the first two cases, although it is relatively high in the cerous oxidation. It is noteworthy that the treatment predicts that, with increasing concentration of substrate, a limiting yield should be approached asymptotically, as is found in practice, and it further indicates that in the cerous case a minimum concentration of 0.013N is necessary for any net oxidation yield; the experimental value is ca. 0.01N.

With increase of pressure the area of the glow spot diminishes and it would be expected that  $[\text{OH}]$  and  $[\text{H}]$  might increase. In general, therefore,  $G$  should diminish with rise of pressure, but the effect will be very dependent on the concentration of substrate chosen, sensitivity to pressure change being only marked at low concentrations. Furthermore from the expressions deduced, the effect should be least with ferrous sulfate and greatest with cerous sulfate. Qualitatively these predictions seem to be in agreement with experimental results.

Thus the above scheme seems able to account in general terms for many features of oxidation in glow-discharge electrolysis but it encounters very great difficulties in the potassium ferrocyanide case. This oxidation shows a number of peculiar features; in particular,  $G$  is linearly dependent on ferrocyanide

anide concentration over a considerable range, and the limiting value is not approached asymptotically but is attained abruptly at a ferrocyanide concentration of 0.125*N*. Furthermore the presence of chloride ion does not materially diminish the oxidation yield, whereas in other cases it always seems to interfere with oxidation by the OH radical (7). A hypothesis which would go some way toward explaining these features might suggest that by virtue of its high negative charge the  $\text{Fe}(\text{CN})_6^{4-}$  ion can act as a scavenger within the primary zone for  $\text{H}_2\text{O}^+$  ions which, as indicated in Eq. (a), may be precursors of the OH radicals produced by dissociation of water molecules. On this basis the probability of a  $\text{H}_2\text{O}^+$  ion reacting before decomposing would be directly proportional to the ferrocyanide concentration, and at a particular concentration all the  $\text{H}_2\text{O}^+$  ions might react within their average life period. This can only be regarded as highly speculative at present, but in view of its peculiar features a study of the ferrocyanide system using the ordinary methods of radiation chemistry might prove highly rewarding.

The scheme of reactions put forward above to account for the mechanism of glow-discharge oxidation must obviously be a somewhat arbitrary simplification of the actual position. Thus in the radiation chemistry of aqueous systems in recent years it has been realized (8) that in addition to the OH and H radicals formed a "molecular" yield of  $\text{H}_2\text{O}_2$  and  $\text{H}_2$  may emerge from the primary zone. This may possibly be so in glow-discharge electrolysis also; indeed the assumption of a primary yield of  $\text{HO}_2$  (rather than  $\text{H}_2\text{O}_2$ ) accompanying the OH radical, which has been regarded as the main oxidizing agent, will explain some of the fine details of the present results which are otherwise obscure;  $\text{HO}_2$  radicals might also arise, of course, by interaction of OH radicals with  $\text{H}_2\text{O}_2$  molecules. It may also be noted that in the reactions suggested no reducing properties have been attributed to the hydrogen atoms formed in the dissociation of water molecules. This is in agreement with what has generally been found in glow-discharge electrolysis; thus the oxidation of a ferrous salt proceeds to completion independently of the concentration of ferric ions present and, even when a glow-discharge cathode is used, very little reduction of a ferric sulfate solution can be brought about. This absence of reducing power in a system in which the existence of hydrogen atoms is postulated has been noted frequently in the radiation field, and much ingenuity has been directed to explaining it (9).

The striking analogy between the results of glow-discharge electrolysis and the action of ionizing radiations is apparent from the previous discussion. Although the energies of the bombarding particles in glow-discharge electrolysis are relatively small, it is to be noted that the dose-rate can be extremely high. Thus with a current of 75 ma, the number of univalent gaseous ions reaching the solution surface per minute is  $2.8 \times 10^{19}$  and, assuming them to have an average energy of 100 ev, this corresponds to a dose-rate of  $2.8 \times 10^{21}$  ev/min. In view of the low energy of the particles very little penetration of the

solution will occur, and the reaction zone immediately under the glow-spot will have a very small volume; thus the dose-rate per unit volume will probably be much greater than the above figure. The ionizing radiations employed in conventional radiochemistry are of much higher energies ( $10^4$  to  $10^6$  ev) than the positive ions in glow-discharge electrolysis, but the dose-rates which can be attained are much lower, being of the order of  $10^{16}$ - $10^{20}$  ev/cc-min. In spite of these differences the chemical effects appear to be closely similar and, if the bombarding particles in glow-discharge electrolysis are assigned energies of about 100 ev, the yields are quantitatively comparable with those produced by  $\alpha$ -particles. This illustrates very forcibly the indirect nature of the chemical reactions produced.

In the present work the study of glow-discharge electrolysis has been limited deliberately to very simple systems in order to clarify the fundamental mechanism, but it is apparent that the method may provide a useful tool for electro-organic preparations. It gives a means of producing and maintaining a very high local concentration of OH radicals in aqueous systems, although the considerable heat dissipated in the discharge may cause experimental difficulty where thermally unstable substances are to be used. There is the possibility also of adapting the technique to nonaqueous media where the reactions of different radical fragments of solvent molecules might be utilized.

Manuscript received Oct. 30, 1957. This paper was prepared 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 1958 JOURNAL.

#### REFERENCES

1. J. Gubkin, *Ann. Physik*, **32**, 114 (1887); K. Klüpfel, *ibid.*, **16**, 574 (1905); A. Makowetsky, *Z. Elektrochem.*, **17**, 217 (1911).
2. A. Klemenc, *et al.*, *Z. Elektrochem.*, **20**, 485 (1914); **37**, 742 (1931); *Z. physik. Chem.*, **130**, 378 (1927); **154**, 385 (1931); **166**, 343 (1933); **27B**, 369 (1935); **179**, 1 (1937); **182**, 91 (1938); **40B**, 252 (1938); **183**, 217, 297 (1938); *Z. anorg. Chem.*, **240**, 167 (1939); *Monatsh.*, **75**, 42 (1944); **76**, 38 (1946); **78**, 243 (1948); **81**, 122 (1950); **82**, 708, 869, 1041 (1951); **84**, 365, 498, 1053 (1953); *Chimia*, **6**, 177 (1952); *Z. Elektrochem.*, **56**, 198, 634, 917 (1952); **57**, 615 (1953); see also, W. R. Cousins, *Z. physik. Chem.*, **4B**, 440 (1929); N. Thon, *Compt. rend.*, **197**, 1114 (1933); W. Braumbek, *Z. Physik.*, **91**, 184 (1934); A. Hickling, *J. Chem. Soc.*, **1934**, 1772; F. Fichter and K. Kestenholz, *Helv. Chim. Acta*, **23**, 209 (1940); V. I. Pavlov, *Compt. rend. Acad. Sci. U.S.S.R.*, **43**, 236, 383, 385 (1944); P. de Beco, *Compt. rend.*, **207**, 623 (1938); **208**, 797 (1939); *Bull. soc. chim.*, **12**, 779, 789, 795 (1945); A. Muta, *J. Electrochem. Soc. Japan*, **17**, 265, 298 (1949).
3. R. A. Davies and A. Hickling, *J. Chem. Soc.*, **1952**, 3595.
4. A. Hickling and J. K. Linacre, *ibid.*, **1954**, 711.
5. H. A. Barton and J. H. Bartlett, *Phys. Rev.*, **31**, 823 (1928); H. D. Smyth and D. W. Mueller, *ibid.*, **43**, 116 (1933); M. M. Mann, A. Hustrulid, and J. T. Tate, *ibid.*, **58**, 340 (1940).
6. Cf. R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).
7. Cf. M. Haissinsky, *J. Chim. phys.*, **53**, 542 (1956); T. J. Sworski, *Radiation Research*, **2**, 26 (1955).
8. A. O. Allen, *Disc. Faraday Soc.*, **12**, 79 (1952).
9. Cf. M. Haissinsky, *ibid.*, 133.

# Vapor Pressure of Titanium Tetrabromide

Elton H. Hall, John M. Blocher, Jr., and Ivor E. Campbell

Battelle Memorial Institute, Columbus, Ohio

## ABSTRACT

Measurements were made of the vapor pressure of  $\text{TiBr}_4(l)$ . The following results were obtained:

$$\text{TiBr}_4(l) = \text{TiBr}_4(g) \\ \log P_{\text{atm}} = \frac{-3706.29}{T} - 6.2424 \log T + 24.199$$

$$P = 1 \text{ atm at } 506.6^\circ\text{K}$$

$$\Delta H_{298.2} = 13.22 \pm 0.10 \text{ kcal}$$

$$\Delta H_{500.0} = 10.60 \pm 0.10 \text{ kcal}$$

$$\Delta S_{298.2} = 27.58 \pm 0.22 \text{ e. u.}$$

$$\Delta S_{500.0} = 20.93 \pm 0.22 \text{ e. u.}$$

Combination of the above data and thermal data with the calculated entropy of  $\text{TiBr}_4(g)$  gave the standard entropy:

$$\text{TiBr}_4(s), S^\circ_{298.2} = 57.6 \pm 0.22 \text{ e. u.}$$

This value agrees with Kelley's value  $57.2 \pm 0.9$  e. u. obtained from low temperature heat-capacity measurements.

Data in the literature on the vapor pressure of  $\text{TiBr}_4$  are inconsistent. Seki (1) measured the vapor pressure of solid and liquid  $\text{TiBr}_4$  over a limited range.<sup>1</sup> However, when his equation for the liquid vapor pressure is corrected for the  $\overline{\Delta C_p}$  of vaporization,  $-12.4$  cal/mole/deg,<sup>2</sup> and extrapolated to 760 mm,  $241^\circ\text{C}$  is obtained for the boiling point. This is inconsistent with the various measured boiling points which converge around  $230^\circ\text{C}$ .<sup>3</sup> Of these, the value of Bond and Crone,  $230^\circ\text{C}$  at 751 mm of Hg, appears to be the most reliable.

Also in disagreement with Seki's results are data obtained in early work at Battelle (8). These data, taken with an isoteniscope (9), were subjected to a statistical analysis which indicated a high degree of precision, but gave a value of  $\overline{\Delta C_p} = -7.574$ , indicated by the coefficient of  $\log T$  in the best fit equation, which did not agree with the expected value of  $\overline{\Delta C_p} = -12.4$ .

Later, Kato and Abe (10) measured the vapor pressure of the liquid in the range 40 to 366 mm with a glass spoon (Bourdon) gauge.<sup>4</sup> Their pressures are significantly lower than either the isoteniscope data or the extrapolation of Seki's data. The data of Kato and Abe are too scattered and the range too narrow to draw any conclusions concerning the magnitude of the  $\overline{\Delta C_p}$  term.

<sup>1</sup> Those referring to Seki's paper should note that several of the vapor pressure tables are mislabeled. The vapor pressure data for  $\text{CBr}_4$ ,  $\text{TiBr}_4$ ,  $\text{SnBr}_4$ , and  $\text{SnI}_4$  are actually presented in Tables I through VIII in the same order as listed in Table IX. Furthermore, the  $\Delta F$  and  $\Delta S$  values listed in Table IX are misleading, having been obtained by multiplying the  $\log P$  equation by 2.303 R without having first converted from mm of Hg to atmospheres. Thus, they imply a standard-state pressure of 1 mm of Hg. The glass-spring manometer used for these measurements is described by Nitta and Seki (2).

<sup>2</sup> See calculation of  $\Delta C_p$  below.

<sup>3</sup> Values have been reported by Blitz and Jeep (3),  $230^\circ\text{C}$  at 761 mm; Bond and Crone (4),  $230^\circ\text{C}$  at 751 mm; Baxter and Butler (5),  $230^\circ\text{C}$  (760 mm ?); Young and Schumb (6),  $230^\circ\text{C}$  (760 mm); and by Olsen and Ryan (7),  $228^\circ\text{C}$  (761 mm).

<sup>4</sup> It should be noted that the value  $\Delta S = 35.73$  e.u. shown in Table I of Kato's paper was obtained by multiplying the  $\log P$  equation by 2.303 R without having first converted from mm of Hg to atmospheres.

A source of error in the spoon-gauge data of Kato and Abe was thought to be the existence of a temperature differential between the bath and the convection-cooled spoon. It was also suspected that the observed  $\overline{\Delta C_p}$  discrepancy in the isoteniscope data might be explained by the possible presence of small amounts of residual moisture in the glass equipment resulting in volatile hydrolysis products.

In order to determine the magnitude of these effects, new data were obtained with a Pyrex spoon gauge. The new data show that the conflicting results can be explained adequately on the above bases.

### Heat Capacity and Standard Entropy of $\text{TiBr}_4$ Vapor

The entropy and heat capacity of  $\text{TiBr}_4$  vapor were calculated from the vibrational frequencies in  $\text{cm}^{-1}$  given by Delwaille, *et al.*, (11). Only the translational, rotational, and vibrational contributions to the energy were considered to be significant. No correction was made for anharmonicity, the effect having been considered to be negligible.

In calculating the rotational contributions, the value given by Lister and Sutton (12) for the Ti-Br distance (2.31 Å) was used. The calculations led to

$$S^\circ_{298.2} = 95.02 \text{ e. u.}$$

and the heat capacities given in Table I. At  $298.2^\circ\text{K}$  and above, the calculated heat capacity can be expressed to within  $\pm 0.02$  cal/mole/deg over most of the range by the equation

$$C_p = 25.77 - 1.58 \times 10^5 T^{-2} \quad (I)$$

where

$$T \geq 298.2^\circ\text{K}$$

At  $400^\circ\text{K}$ , the equation is in error by 0.04 units.

Since these calculations were made, similar calculations by Skinner, Johnston, and Beckett have

Table I. Heat Capacity of TiBr<sub>4</sub>(g)

Temp, °K	C <sub>p</sub> , calculated cal/mole/deg	C <sub>p</sub> , Eq. (I)
200	22.35	(21.82)
300	24.02	24.01
400	24.74	24.78
500	25.12	25.14
700	25.45	25.45

Table II. Vapor Pressure of Liquid TiBr<sub>4</sub>

Sample	T, °K	P <sub>TiBr<sub>4</sub></sub> , mm Hg	log P <sub>obs</sub> - log P <sub>calc</sub> †
A	352.1	5.9	+0.1144
A	383.7	21.4	+0.0441
A	413.0	62.8	+0.0188
A	336.8	3.1	+0.1927
A	362.5	9.3	+0.0889
A	372.9	14.6	+0.0764
A	393.2	31.5	+0.0409
A	428.1	101.5	+0.0109
B	446.3	175.7	+0.0062
B	431.8	113.7	+0.0099
B	453.0	211.6	+0.0076
B	465.8	290.4	-0.0042
B	480.5	424.4	+0.0014
B	472.7	347.6	-0.0023
B	459.0	246.4	+0.0024
B	441.0	150.6	+0.0098
D	372.6	11.5	-0.0199
D	387.3	22.3	-0.0068
D	402.2	40.3	-0.0018
D	416.0	65.7	-0.0069
D	403.7	43.4	+0.0061
D	390.9	26.0	-0.0034
D	448.1	181.8	+0.0018
D	472.3	345.9	0.0000
D	498.5	634.7	-0.0025
D	488.4	508.2	-0.0010
D	476.4	381.0	-0.0021
D	464.6	283.2	-0.0013
D	450.8	194.2	-0.0027
D	446.3	171.0	-0.0024
D	436.3	126.9	-0.0029
D	418.2	71.2	-0.0011
D	402.5	41.1	+0.0019
D	387.4	23.1	+0.0067
D	376.4	13.7	-0.0174
D	371.1	10.7	-0.0257
D	366.4	8.6	-0.0271
D	392.9	28.2	-0.0012
D	398.0	34.4	-0.0013
D	414.3	62.5	0.0000
E	401.6	39.4	-0.0018
E	365.2	8.7	+0.0023
E	349.8	3.9	-0.0162
E	356.4	5.4	-0.0204
E	374.5	13.5	+0.0125
E	419.2	73.0	-0.0050
E	452.9	206.4	-0.0019
E	472.4	345.8	-0.0012
E	463.4	273.9	-0.0023
E	434.2	120.0	+0.0009
E	413.2	60.6	+0.0032
E	407.6	49.4	+0.0012
E	395.6	31.5	+0.0007
E	346.6	3.5	+0.0098
E	355.0	5.5	+0.0179
E	363.6	7.8	-0.0123
F	358.6	6.6	+0.0197
F	369.3	10.7	+0.0138

Table II. Vapor Pressure of Liquid TiBr<sub>4</sub> (Continued)

Sample	T, °K	P <sub>TiBr<sub>4</sub></sub> , mm Hg	log P <sub>obs</sub> - log P <sub>calc</sub> †
F	374.5	13.5	+0.0125
F	392.2	27.6	0.0000
F	404.4	44.6	+0.0067
F	417.9	70.1	-0.0034
F	429.5	104.2	+0.0035
F	422.2	82.2	+0.0033
F	413.3	60.4	+0.0003
F	400.6	37.9	-0.0023
F	376.7	14.5	+0.0014
F	457.4	234.0	-0.0010
F	456.4	228.1	-0.0014
F	468.4	314.3	+0.0012
F	489.0	516.0	-0.0002
F	481.8	435.5	-0.0007
F	452.1	203.2	+0.0010
F	441.4	150.2	+0.0035
F	354.1	5.1	+0.0048
F	341.2	2.5	-0.0097
F	385.8	21.9	+0.0121
F	354.5	5.1	-0.0039
F-II	404.2	44.2	+0.0060
F-II	444.5	164.4	+0.0032
F-II	432.2	112.8	+0.0008
F-II	487.1	494.6	+0.0005
F-II	474.8	368.6	+0.0005
F-II	460.6	256.2	+0.0009
F-II	359.4	6.9	+0.0220
F-II	370.2	11.0	+0.0079
F-II	376.8	14.9	+0.0112
F-II	384.5	20.2	+0.0026
F-II	395.5	31.8	+0.0065

\* Data listed in the order taken. Pressure corrected for thermal expansion of Hg in the manometer and for latitude.

† Calculated from the equation:  $\log P_{atm} = -3706.29/T - 6.2424 \log T + 24.199$ .

been published (13) which are in essential agreement.

Recent determinations by Kelley (14) show that the heat capacity of liquid titanium tetrabromide is essentially constant between the melting and boiling points. His value, 37.3 cal/mole/deg, is the result of careful determinations and should be quite reliable. Using this value with the heat capacity of the gas obtained from the above equation, one finds a  $\Delta C_p$  of vaporization of -12.4 cal/mole/deg at 420°K, near the middle of the range of vapor-pressure measurements.

### Experimental

The Pyrex spoon gauge, with sample reservoir attached, was submerged in an oil bath thermostat ( $\pm 0.2^\circ\text{C}$ ) whose temperature was measured with a chromel-alumel thermocouple calibrated at the boiling point of water and the melting point of tin.

After the initial bake-out of the gauge and appendages at 450°C and 0.05 $\mu$  pressure overnight, a break seal was broken, and some TiBr<sub>4</sub> was distilled under vacuum through the system. A sample was then condensed in the reservoir and Willard valves (15) on either side were closed. Pressure measurements were made with the spoon gauge used as a null instrument. After the desired data were obtained, proper manipulation of the Willard valves



permitted either partial removal of the sample and re-examination of the residue, or complete removal and replacement by a fresh sample. During Runs D, E, F, and F-II, a heating tape wrapped around the upper part of the outer envelope of the spoon gauge was heated strongly enough to prevent condensation of liquid  $\text{TiBr}_4$  in the spoon itself. For Runs F and F-II, the Willard valves were replaced by capillary tubes which served as valves on condensing and freezing plugs of  $\text{TiBr}_4$ .

The titanium tetrabromide used in Runs A and B was obtained from the National Bureau of Standards. Another sample of the same lot was reported by NBS to have an over-all purity of 99.998 as measured by analysis of the melting curve. The triple point temperature was reported to be  $311.50^\circ \pm 0.01^\circ\text{K}$ . The sample was transferred by vacuum distillation into small ampoules from the large ampoule in which it was shipped. Liquid nitrogen was used to cool the pump trap and the glass was outgassed by flaming with a hand torch. Samples A and B were successive cuts from one small ampoule.

A second lot of tetrabromide, received from the Bureau of Standards having the same purity specifications, was also transferred to small ampoules. In order to eliminate, if possible, any traces of residual moisture, a seasoning technique was adopted. The transfer system was evacuated to  $<0.01\mu$  and heated to about  $150^\circ\text{C}$  for 24 hr, after which it was then flushed out with a sample of redistilled tetrabromide so that all of the glass was in prolonged contact with the liquid. The material was all distilled out before the NBS sample was transferred. The first fraction, Sample C, from one small ampoule was used to precondition the glass surfaces of the gauge. After being heated for 48 hr, the  $\text{TiBr}_4$  was entirely removed by volatilization. Samples D and E were subsequent cuts from the same ampoule, while Sample F was from a second ampoule. F-II designates the sample remaining after about half of F was removed by distillation.

Pressure vs. temperature data for the six separate samples are presented in Table II. The mutually consistent data from Samples D, E, F, and F-II were subjected to a  $\Sigma$ -calculation in which the coefficient of  $\log T$  in the vapor-pressure equation was assigned the value  $-6.2424$  ( $\overline{\Delta C_p} = -12.4$ ). This treatment leads to the equation:

$$\log P_{\text{atm}} = -3706.29/T - 6.2424 \log T + 24.199$$

In the fourth column of Table II are listed the deviations of each point from the above equation. A plot of the deviations vs.  $T$ ,  $^\circ\text{K}$  is shown in Fig. 1. It may be seen that the data for Samples D, E, F, and F-II are randomly scattered about zero deviation; hence, the value of  $\overline{\Delta C_p} = -12.4$  is consistent with these data. Data for Samples A and B do not agree with the other four samples. For purposes of comparison, it may be noted that the best equation through the data of A and B is actually a straight line, i.e., the apparent  $\Delta C_p = 0$ . Also shown in Fig. 1 are the deviations of the data of Seki, Kato, and

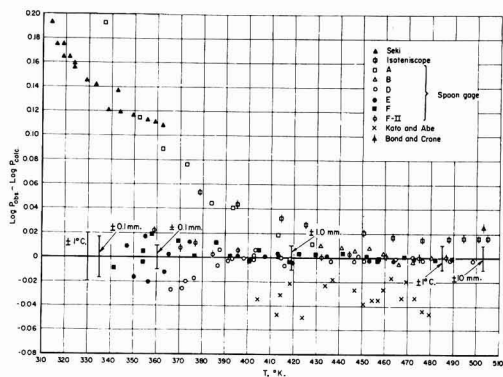


Fig. 1. Vapor pressure of liquid  $\text{TiBr}_4$ . Deviation from  $\log P_{\text{atm}} = -3706.29/T - 6.2424 \log T + 24.199$ .

Abe, the isotenoscope data, and the boiling point of Bond and Crone.

### Discussion

Two differences in the experimental technique have significance in the interpretation of the results: (a) prevention of condensation of  $\text{TiBr}_4$  in the spoon portion of the system during pressure measurements, and (b) preconditioning of all glassware with  $\text{TiBr}_4$ . These precautions were employed for Samples D, E, F, and F-II, but not for A and B.

If liquid is permitted to condense in the spoon as a result of circulation of cool inert gas within the envelope, the equilibrium temperature may be noticeably lower than the bath temperature. In an experiment at constant bath temperature, the observed pressure dropped from 626.4 to 609.9 mm of Hg when the heated envelope was allowed to cool toward room temperature. This pressure difference is equivalent to a temperature difference of  $1.2^\circ\text{C}$ . In the low temperature range of the data, no pressure difference could be observed between a cool and a heated envelope because of the reduced convective effect at low pressure. Kato and Abe do not indicate that any precautions were taken to prevent condensation. However, as can be seen from the deviation plot, correction of their data by the above amount would bring them into better correlation with the data reported here for Samples D, E, F, and F-II. The actual magnitude of the correction would, of course, vary with the geometry of the particular apparatus.

If routine vacuum bakeout of glassware were not successful in removing sorbed moisture completely, subsequent hydrolysis of the tetrabromide would be expected to produce small amounts of volatile hydrolysis products, such as HBr, dissolved in the tetrabromide. This would introduce a rather large positive error in the observed pressure in the low-pressure range, but a much smaller relative error in the high-pressure range. The deviation plot shows that the data from Samples A and B vary in such a manner. Since the differences in sample handling technique should have reduced the possibility of moisture contamination for Samples D, E, F, and F-II, it is likely that residual moisture was indeed

the source of error in the data from Samples A and B. Since Seki's data and the isoteniscope data deviate in the same manner as Samples A and B, the same explanation probably applies.<sup>5</sup>

The fact that the deviation of the data from Sample B in the high-pressure range is smaller than that of the isoteniscope data is probably the result of compensating errors. The impurity error would lead to positive deviation, while the condensation error would lead to negative deviation.

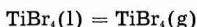
The absence of volatile or soluble nonvolatile impurities in Sample F is shown by the fact that after volatilization of about half of the sample the vapor pressure remained unchanged.

### Results

One has a choice of two methods for treatment of the data. The free energy and enthalpy functions may be constructed from the  $C_p$  data of Kelley (14) and the spectroscopic data of Dewaulle, *et al.* (11), which permit the calculation of values of  $\Delta H^\circ$  for each experimental vapor-pressure point. The consistency of the data is then judged by the absence of scatter and of trend with temperature in the  $\Delta H^\circ$  values.

For the present purpose, and in view of the fact that the  $C_p$  data of Kelley are as yet unpublished, the authors prefer the  $\Sigma$ -function treatment which gives convenient analytical expressions for the results. The consistency with the Third Law can be tested by comparing the entropies of vaporization calculated from the vapor-pressure data and from the thermal data. Agreement of the thermodynamic quantities calculated by the two methods is well within the precision of the data.

Treatment of the data from Samples D, E, F, and F-II by the method of least squares leads to the following results for



$$\log P_{\text{atm}} = -3706.29/T - 6.2424 \log T + 24.199$$

$$P = 1 \text{ atm at } 506.6^\circ\text{K} \text{ (233.4}^\circ\text{C)}$$

The indicated normal boiling point,  $233.4^\circ\text{C}$ , is  $2.6^\circ$  above the  $230.8^\circ\text{C}$  (corrected) given by Bond and Crone (4), *i.e.*, about  $3^\circ\text{C}$  above the several values previously reported. However, recent unpublished results of Johannesen (16) at the National Bureau of Standards tend to confirm the higher value obtained in the present work. In the distillation of a sample of  $\text{TiBr}_4$ , Johannesen obtained a final boiling point of  $232^\circ\text{C}$  at 765 mm of Hg with a calibrated thermometer totally immersed in the vapor. Since the boiling point had risen  $1^\circ\text{C}$  during the distillation, it was suspected that the  $\text{TiBr}_4$  contained some residual  $\text{TiCl}_4$  from the preparation and that the value  $232^\circ\text{C}$  is somewhat low.

The ratio of fugacity<sup>6</sup> to pressure as a function of temperature may be approximated in the range of the data by the equation

$$\log f/p = -0.0738 \log T + 0.1908$$

By addition to the above equation one obtains,

$$\log f_{\text{atm}} = -3706.29/T - 6.3162 \log T + 24.390$$

from which the following thermodynamic quantities are derived:

$$\overline{\Delta C_p} = -12.54 \text{ cal/mole/deg}$$

$$\Delta H_{506.6} = 13.22 \pm 0.10 \text{ kcal}$$

$$\Delta H_{506.6} = 10.60 \pm 0.10 \text{ kcal}$$

$$\Delta S_{506.6} = 27.58 \pm 0.22 \text{ e. u.}$$

$$\Delta S_{506.6} = 20.93 \pm 0.22 \text{ e. u.}$$

The uncertainties are expressed as the maximum deviation from the mean of the values obtained by separate treatment of the data from each sample.

It is recognized that the coefficient of  $\log T$  in the fugacity equation is the  $\overline{\Delta C_p}/R$  which should be compared with that obtained from the  $C_p$  of the gas and liquid as previously described. The indicated value  $\overline{\Delta C_p} = -12.54$  is the difference between the gas and liquid at  $400^\circ\text{K}$ . Since this temperature is still near the middle of the range of the data and the temperature taken for the  $\overline{\Delta C_p}$  calculation is somewhat arbitrary in any case, the  $\overline{\Delta C_p}$  indicated by the fugacity equation is considered to be as appropriate for the present purpose.

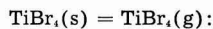
The above data can be used to obtain an equation for the vapor pressure of the solid. In addition to its inherent interest, this permits a comparison of the entropy of the solid with that obtained calorimetrically by Kelley (18). The heat of fusion of  $\text{TiBr}_4(s)$ ,  $\Delta H_m = 3080 \text{ cal/mole}$  (14) is added to the heat of vaporization of the liquid at the melting point,  $\Delta H_{511.4} = 13,051 \text{ cal/mole}$ , as calculated from the fugacity equation above, to obtain the heat of sublimation at the melting point,  $\Delta H_{511.4} = 16,131 \text{ cal/mole}$ . This value is extrapolated to  $0^\circ\text{K}$  with the value  $\overline{\Delta C_p} = -7.5 \text{ cal/mole/deg}^7$  to give  $\Delta H^\circ = 18,467 \text{ cal/mole}$ .

The above values can be substituted in an equation of the form:

$$4.575 \log P = -\Delta H^\circ/T + 2.303 \overline{\Delta C_p} \log T - I$$

the value of  $I$  being determined by substituting, for  $P$ , the value calculated at the melting point from the equation for the vapor pressure of the liquid.

This treatment leads to the following results for



$$\log P_{\text{atm}} = -4036.5/T - 3.776 \log T + 19.106$$

$$\overline{\Delta C_p} = -7.5 \text{ cal/mole/deg}$$

$$\Delta H_{506.2} = 16.2 \text{ kcal}$$

$$\Delta H_{511.4} = 16.1 \text{ kcal}$$

$$\Delta S_{506.2} = 37.2 \text{ e. u.}$$

$$\Delta S_{511.4} = 36.8 \text{ e. u.}$$

The derived equation for solid  $\text{TiBr}_4$  gives pressures about 50% lower than those observed by Seki for the vapor pressure of the solid. The difference may be attributable to the presence of hydrolysis products in Seki's material.

<sup>7</sup> Kelley (18) gives  $31.43 \text{ cal/mole/deg}$  for the heat capacity of solid  $\text{TiBr}_4$  at  $298.2^\circ\text{K}$ . At the same temperature  $C_p(g) = 23.9 \text{ cal/mole/deg}$  is obtained from spectroscopic data, as discussed above.

<sup>5</sup> It may be noted that the deviation of the isoteniscope data, for example, is not quantitatively accounted for at both ends of the pressure range on the basis of an ideal solution of  $\text{HBr}$  in  $\text{TiBr}_4$ . However, since the qualitative explanation appears adequate, consideration of uncertain departure from ideality in an effort to improve the agreement did not seem to be justified.

<sup>6</sup> Estimated by the method of Brewer and Searcy (17).

The above value of  $\Delta S_{298.2}$  may be combined with the standard entropy of  $\text{TiBr}_4(\text{g})$ ,  $S^\circ_{298.2} = 95.02$  e. u., corrected by  $-0.2$  e. u. for nonideality,<sup>8</sup> to give for  $\text{TiBr}_4(\text{s})$  at  $298.2^\circ\text{K}$

$$S^\circ_{298.2} = 57.6 \text{ e. u.}$$

The agreement with Kelley's (18) value of  $57.2 \pm 0.9$  e. u., obtained from low temperature heat-capacity measurements, is within the ascribed uncertainty.

#### Acknowledgment

The authors are grateful for the help and interest of the Office of Naval Research who supported this work under Contract Nonr-1120(00) as part of their program on the extractive metallurgy of titanium.

Manuscript received Oct. 14, 1957. This paper was prepared for delivery before the Cleveland Meeting, Sept. 30-Oct. 4, 1956.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1958 JOURNAL.

#### REFERENCES

1. S. Seki, *J. Chem. Soc. Japan*, **62**, 789 (1941).
2. I. Nitta and S. Seki, *ibid.*, **62**, 581 (1941).
3. W. Biltz and K. Jeep, *Z. anorg. Chem.*, **162**, 32 (1927).

<sup>8</sup> On the basis of comparison with tin tetrachloride, for which a correction of  $-0.16$  e. u. is estimated from the critical constants, as suggested by Kelley, private communication, April, 1956.

4. P. A. Bond and E. B. Crone, *J. Am. Chem. Soc.*, **56**, 2028 (1934).
5. G. P. Baxter and A. Q. Butler, *ibid.*, **50**, 408 (1928).
6. R. C. Young and W. C. Schumb, *ibid.*, **52**, 4233 (1930).
7. J. B. Olsen and E. P. Ryan, *ibid.*, **54**, 2215 (1932).
8. J. M. Blocher, Jr., R. F. Rolsten, N. D. Veigel, and I. E. Campbell, Technical Report on "The Preparation and Properties of Titanium Tetrabromide" to ONR from Battelle Memorial Institute, Contract Nonr-1120(00) July 1, 1955.
9. A. Smith and A. W. C. Menzies, *J. Am. Chem. Soc.*, **32**, 1412 (1910).
10. H. Kato and M. Abe, *J. Chem. Soc. Japan*, **76**, 1182 (1955).
11. M. L. Delwaille and F. Francois, *Compt. rend.*, **220**, 173 (1945).
12. M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **37**, 393 (1941).
13. G. Skinner, H. L. Johnston, and C. Beckett, "Titanium and Its Compounds," p. 111, Herrick L. Johnston Enterprises, Columbus, Ohio (1954).
14. K. K. Kelley, Quarterly Status Report to ONR from the U. S. Bureau of Mines, Project NR 037-054, October-December, 1955.
15. J. Willard, *J. Am. Chem. Soc.*, **57**, 2328 (1935).
16. R. B. Johannesen, Private communication, Sept. 30, 1957.
17. L. Brewer and A. W. Searcy, *J. Chem. Ed.*, **26**, 548 (1949).
18. K. K. Kelley, Quarterly Status Report to ONR from U. S. Bureau of Mines, Project NR 037-054, July-September 1955.

## Vapor Pressure of Titanium Tetrafluoride

Elton H. Hall, John M. Blocher, Jr., and Ivor E. Campbell

*Battelle Memorial Institute, Columbus, Ohio*

#### ABSTRACT

Measurements were made of the vapor pressure of  $\text{TiF}_4(\text{s})$ . The following results were obtained:

$$\begin{aligned} \text{TiF}_4(\text{s}) &= \text{TiF}_4(\text{g}) \\ \log P_{\text{atm}} &= -5331.51/T - 2.567 \log T + 16.631 \\ P &= 1 \text{ atm at } 556.3^\circ\text{K} \\ \Delta H_{298.2} &= 22.87 \pm 0.28 \text{ kcal} \\ \Delta H_{556.3} &= 21.55 \pm 0.28 \text{ kcal} \\ \Delta S_{298.2} &= 41.92 \pm 0.40 \text{ e. u.} \\ \Delta S_{556.3} &= 38.74 \pm 0.40 \text{ e. u.} \end{aligned}$$

Combination of the above data and thermal data with the calculated entropy of  $\text{TiF}_4(\text{g})$ ,  $S^\circ_{298.2} = 73.2$  e. u., gave the standard entropy:

$$\text{TiF}_4(\text{s}), S^\circ_{298.2} = 31.3 \pm 0.40 \text{ e. u.}$$

Ruff and Plato (1) obtained  $284^\circ\text{C}$  as the normal sublimation point of  $\text{TiF}_4$  by measuring the temperature of the vapor subliming at atmospheric pressure in a platinum flask, but no other experimental data relative to the vapor pressure of  $\text{TiF}_4$  are available in the literature.

To provide these data and to derive related thermodynamic quantities, the vapor pressure has been measured over the temperature range  $430^\circ$  to  $560^\circ\text{K}$ .

#### Materials

The  $\text{TiF}_4$ , obtained from General Chemical Division, Allied Chemical and Dye Corporation, was purified by high vacuum ( $p = 0.01\mu$ ) sublimation

from a Pyrex boiler to a Pyrex receiver fitted with a break seal. The trap to the vacuum system was cooled in liquid nitrogen.<sup>1</sup>

Analysis of a sample of commercial  $\text{TiF}_4$  sublimed in this manner gave a F/Ti ratio of 3.93. The 1.7% deviation from the theoretical value is within the uncertainty of the fluorine analysis and in the direction of the expected error. Spectrographic analysis showed less than 0.005% Si and less than 0.015% total metallic impurity.

The absence of reaction between dry  $\text{TiF}_4$  and Pyrex glass in the temperature range employed is

<sup>1</sup> It should be noted that cooling the trap with dry ice-acetone is an insufficient precaution against hydrolysis and subsequent discoloration of the  $\text{TiF}_4$  on heating.

indicated by (a) absence of visible etching, (b) low (0.005%) Si content of the  $TiF_4$ , (c) reproducible pressure data, (d) absence of noncondensable gases on condensation of the  $TiF_4$ , and (e) agreement of the pressure data obtained in glass and in copper systems.

Transfer of the  $TiF_4$  to the measuring cell was made by sublimation under vacuum or directly under an inert gas blanket.

### Vapor Pressure Measurements

Four methods were employed in the measurement of the vapor pressure; spoon (Bourdon) gauge method, the Ruff-Fischer method summarized by Kubaschewski and Evans (2), the transpiration, or gas-saturation method, and the method of Rodebush and Dixon (3). The first is a static method while the others are dynamic methods.

The Pyrex spoon gauge was used as a null instrument, the vapor pressure of  $TiF_4$  on the inside of the gauge being balanced by a measured pressure of argon on the outside. The gauge was immersed in a salt bath thermostat ( $\pm 0.2^\circ C$ ) the temperature of which was measured with a calibrated chromel-alumel thermocouple.

In spite of an initial bakeout in vacuum, some outgassing sometimes occurred during the first stages of a run. The residual gases were pumped out through a Willard valve (4) provided for the purpose. Data were not retained unless zero residual pressure was observed on cooling the cell.

The data obtained for two different samples (Runs A and B) are given in Table I and Fig. 1.

The second method employed was first used by Ruff (5) and later improved by Fischer (6). The determination is made by varying the pressure over a sample held at constant temperature. A sharp change in the observed rate of evaporation determines the point at which the measured opposing pressure equals the vapor pressure.

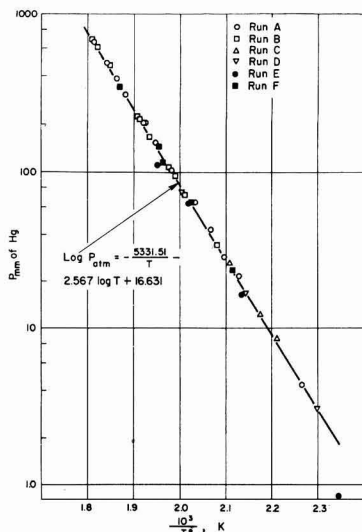


Fig. 1. Vapor pressure of  $TiF_4$ .

Table I. Vapor pressure of  $TiF_4$ .

Sample	Method	Temp, °K	$P_{TiF_4}^*$ mm Hg	$\log P_{Obs} - \log P_{Calc}$
A	Spoon gauge	492.4	63.6	+0.031
A	Spoon gauge	520.8	203.7	+0.008
A	Spoon gauge	520.4	201.0	+0.009
A	Spoon gauge	537.4	382.7	+0.001
A	Spoon gauge	551.7	653.6	+0.005
A	Spoon gauge	543.7	479.9	-0.003
A	Spoon gauge	532.0	308.1	-0.004
A	Spoon gauge	513.7	149.8	+0.001
A	Spoon gauge	504.3	101.4	+0.005
A	Spoon gauge	483.7	42.4	+0.029
A	Spoon gauge	476.7	28.4	+0.002
A	Spoon gauge	470.2	21.6	+0.021
A	Spoon gauge	441.4	4.3	-0.013
B	Spoon gauge	480.4	33.7	-0.002
B	Spoon gauge	516.1	163.9	-0.003
B	Spoon gauge	496.9	69.7	-0.017
B	Spoon gauge	505.8	105.7	-0.006
B	Spoon gauge	523.0	213.0	-0.011
B	Spoon gauge	535.2	343.0	-0.010
B	Spoon gauge	493.2	62.9	+0.010
B	Spoon gauge	502.4	92.4	0.000
B	Spoon gauge	522.2	212.5	+0.002
B	Spoon gauge	531.8	303.6	-0.007
B	Spoon gauge	542.2	459.1	+0.002
B	Spoon gauge	549.9	603.3	-0.001
B	Spoon gauge	552.6	666.5	0.000
C	Ruff-Fischer	474.3	26.0	+0.013
C	Ruff-Fischer	452.4	8.4	+0.017
C	Ruff-Fischer	460.2	11.6	-0.025
D	Ruff-Fischer	435.4	3.1	-0.004
D	Ruff-Fischer	466.9	16.5	-0.023
D	Ruff-Fischer	498.8	74.2	-0.027
E	Transpiration	426.2	0.83	-0.333
E	Transpiration	468.2	16.1	-0.063
E	Transpiration	512.2	109.0	-0.111
F	Rodebush	472.9	23.5	-0.015
F	Rodebush	493.5	63.5	+0.008
F	Rodebush	495.7	63.5	-0.035
F	Rodebush	512.0	144.0	+0.014
F	Rodebush	509.5	115.0	-0.038
F	Rodebush	537.4	387.0	+0.005

\* Pressures corrected for thermal expansion of mercury in the manometer and for latitude.

† From the equation:  $\log_{10} P_{atm} = -5331.51/T - 2.567 \log T + 16.631$ .

The data obtained for two different samples (Runs C and D) are given in Table I and Fig. 1.

The third method employed an all-metal transpiration system. The three points (Run E), given in Table I and Fig. 1, were determined by Sense of Battelle. Details of the technique have been reported by Sense, *et al.* (7).

An additional correlation was sought in data taken in a metal system by the "quasi-static" method of Rodebush and Dixon (3, 8). All parts of the Rodebush cell in contact with  $TiF_4$  vapor were made of copper. Waxed tapered seals to Pyrex were made at the cooled appendages.

The cell was heated in an air bath and the temperature measured with a calibrated chromel-alumel thermocouple. Power to the furnace was hand controlled to a temperature variation of less than  $\pm 0.8^\circ C$ .

The  $TiF_4$  vaporizing from the cell was totally condensed in the copper tube outside the furnace and, therefore, did not come in contact with the glass portion of the system.

In the experiments reported, it was not found possible to obtain a permanent difference in the levels of the differential manometer. It was observed, however, that the magnitude of the inert pressure relative to the vapor pressure caused considerable variation in the length of time required for the manometer to return to zero differential after a given volume of inert gas had been removed from one side. The slow recovery is attributed to evaporative cooling of the sample. This is not noticed when dealing with liquids because of the much more efficient heat transfer to the sample.

The following modification of the Rodebush technique was adopted. With the sample at constant temperature and the inert pressure greater than the expected vapor pressure, a small controlled amount of inert gas was pumped out, and the time required for the manometer to return to zero (recovery time) was determined. The procedure was repeated three or four times and the average recovery time and the inert pressure recorded. The inert gas pressure was then reduced by about 5 mm and the average recovery time determined at the new pressure. The process was repeated at successively lower pressures until the inert pressure was below the vapor pressure, as indicated by the increased recovery time. The pressure was then plotted against the recovery time and the points joined by two intersecting lines. The pressure at the point of intersection was taken as equal to the vapor pressure. The data, Run F, are given in Table I, and Fig. 1.

### Discussion of Results

In Fig. 1, the data from all four methods are shown on a  $\log P_{\text{mm.}}$  vs.  $1/T^{\circ}\text{K}$  plot, while in Fig. 2 the deviation ( $\log P_{\text{obs.}} - \log P_{\text{calc.}}$ ) is plotted vs. temperature. The Ruff-Fischer data are seen to be in good agreement with the spoon-gauge data. It is to be noted that the most probable errors in the spoon-gauge method, namely formation of  $\text{HF}(\text{g})$  or  $\text{SiF}_4(\text{g})$  by residual water in the  $\text{TiF}_4$ , or outgassing of the sample, would tend to make the observed pressures too high since it is a total pressure method, while the largest error in the Ruff-Fischer method, which is thought to be the temperature differential between the bath and the evaporation-cooled sample, would lead to values which are too low. The fact that both sets of data fall on the same line strongly indicates that these systematic errors are smaller than random errors from other sources.

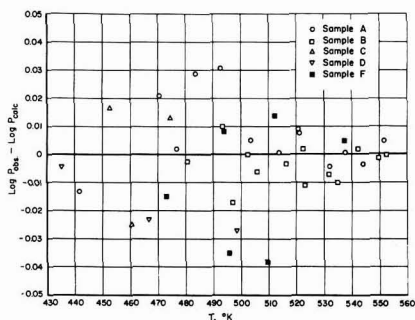


Fig. 2. Vapor pressure of  $\text{TiF}_4$ . Deviation from  $\log P_{\text{atm}} = -5331.51/T - 2.567 \log T + 16.631$ .

The transpiration data are in general agreement with the other, although all three values are low. At the high-pressure point, the condenser tended to clog, while, at the lower points, the loosely adherent condensate was subject to entrainment in the inert-gas stream. Both conditions would lead to low results and it was concluded that the experimental error was large enough to account for the deviations observed. Further refinement of the technique as applied to  $\text{TiF}_4$ , did not appear to be warranted.

It will be noted that the data obtained by the Rodebush method are in good agreement with the spoon-gauge data, indicating that errors introduced by contamination in using a glass system are insignificant. Since the Rodebush method was employed primarily as a check on the spoon-gauge data, the precision sought was not high. Therefore, these data were not included in the statistical analysis.

A sample correction of vapor pressure to fugacity by an approximate method suggested by Brewer and Searcy (9) was found to alter the calculated heat of vaporization by about 65 cal. Since this is well within the experimental uncertainty in the heat of vaporization, the correction to fugacity was not thought to be justified.

In order to extrapolate the data, a value for  $\Delta C_p$  must be obtained. To calculate an approximate value for the heat capacity of the gas, the vibrational frequencies of  $\text{TiF}_4(\text{g})$  were estimated to be,  $192[2]^2$ ,  $232[3]$ ,  $704[1]$ , and  $804[3]$ , by comparing those given by Kelley (10) for  $\text{CBr}_4$ ,  $\text{CCl}_4$ ,  $\text{CF}_4$ ,  $\text{SiBr}_4$ ,  $\text{SiCl}_4$ ,  $\text{SiF}_4$ , and  $\text{TiCl}_4$ , and by Delwaille, *et al.* (11) for  $\text{TiBr}_4$ . From the estimated frequencies, the heat capacity of the gas at  $500^{\circ}\text{K}$  was calculated [see, for example, Rossini (12)] to be 22.9 cal/mole/deg. For the solid, the variation of the heat capacity as a function of the ratio,  $T/T_{\text{m.p.}}$ , was compared for  $\text{TiBr}_4$  (13) and  $\text{TiCl}_4$  (14). The curves were roughly coincident, and the value, 28.0 cal/mole/deg, for  $\text{TiF}_4(\text{s})$  at  $500^{\circ}\text{K}$  was taken to be 1 cal/mole/deg less than the corresponding  $\text{TiCl}_4$  value to allow for the smaller mass of the fluorine. The resulting  $\Delta C_p = -5.1$  was taken as the average over the range of the data.

The spoon-gauge and Ruff-Fischer data, representing four separate samples, were subjected to a  $\Sigma$ -calculation yielding the following results for

$$\text{TiF}_4(\text{s}) = \text{TiF}_4(\text{g}) : ^3$$

$$\Delta C_p = -5.1 \text{ (estimated)}$$

$$\log P_{\text{atm.}} = -5331.51/T - 2.567 \log T + 16.631$$

$$P = 1 \text{ atm at } 556.3^{\circ}\text{K}, 283.1^{\circ}\text{C}$$

$$\Delta H_{298.2} = 22.87 \pm 0.28 \text{ kcal}$$

$$\Delta H_{556.3} = 21.55 \pm 0.28 \text{ kcal}$$

$$\Delta S_{298.2} = 41.92 \pm 0.40 \text{ e. u.}$$

$$\Delta S_{556.3} = 38.74 \pm 0.40 \text{ e. u.}$$

The uncertainties attached to the experimental heats and entropies of vaporization represent the differences in the values resulting from individual treatment of the data from Runs A and B. The deviations of the experimental data from the equation obtained above are shown in Fig. 2.

<sup>2</sup> The multiplicities are given in brackets.

<sup>3</sup> Vapor density determinations by Ruff and Plato (15) show that  $\text{TiF}_4$  vapor is monomeric at  $444^{\circ}\text{C}$ .



The extrapolated temperature at which the vapor pressure equals one atmosphere may be compared with the value, 284°C, reported by Ruff (1).

The standard entropy of  $\text{TiF}_4(\text{s})$  may be obtained by combining the above data with the standard entropy of  $\text{TiF}_4(\text{g})$  at 298.2°K which can be estimated with reasonable certainty. The rotational contribution to the entropy was calculated by estimating a value of  $1.8 \times 10^{-8}$  cm for the Ti-F distance from comparison of the tetrahalides of carbon, silicon, and titanium. The vibrational frequencies for  $\text{TiF}_4$ , estimated above were used to calculate the vibrational contribution to the entropy.

The calculations give for  $\text{TiF}_4(\text{g})$ :

$$S^\circ_{298.2} = 73.2 \text{ e. u.}$$

which may be combined with the above value for the entropy of sublimation to give for  $\text{TiF}_4(\text{s})$ :

$$S^\circ_{298.2} = 31.3 \text{ e. u.}$$

#### Acknowledgment

The authors are grateful for the help and interest of the Office of Naval Research who supported this work under Contract Nonr-1120(00) as part of their program on the extractive metallurgy of titanium.

Manuscript received Oct. 14, 1957. This paper was prepared for delivery before the Cleveland Meeting, Sept. 30-Oct. 4, 1956.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1958 JOURNAL.

#### REFERENCES

- O. Ruff and W. Plato, *Ber.*, **37**, 673 (1904).
- O. Kubaschewski and E. L. L. Evans, "Metallurgical Thermochemistry," 2nd ed., p. 150, John Wiley & Sons, Inc., New York (1956).
- W. H. Rodebush and A. L. Dixon, *Phys. Rev.*, **26**, 851 (1925).
- J. Willard, *J. Am. Chem. Soc.*, **57**, 2328 (1935).
- O. Ruff and B. Bergdahl, *Z. anorg. chem.*, **106**, 76 (1919).
- W. Fischer and O. Rahlfs, *ibid.*, **205**, 1 (1932).
- K. A. Sense, J. J. Snyder, and R. B. Filbert, Jr., *J. Phys. Chem.*, **58**, 995 (1954).
- E. F. Fiock and W. H. Rodebush, *J. Am. Chem. Soc.*, **48**, 2522 (1926).
- L. Brewer and A. W. Searcy, *J. Chem. Ed.*, **26**, 548 (1949).
- K. K. Kelley, U. S. Bureau of Mines Bull. No. 477 (1950).
- M. L. Delwaille and F. Francois, *Compt. rend.*, **220**, 173 (1945).
- F. D. Rossini, "Chemical Thermodynamics," Chap. 19, John Wiley & Sons, Inc., New York (1950).
- K. K. Kelley, Quarterly Status Report to ONR from U. S. Bureau of Mines, Project NR 037-054, July-September 1955.
- W. M. Latimer, *J. Am. Chem. Soc.*, **44**, 90 (1922).
- O. Ruff and W. Plato, *Ber.*, **37**, 677 (1904).

## Mechanisms of Hydrogen Producing Reactions on Palladium

### V. The Deuterium-Palladium System

Sigmund Schuldiner and James P. Hoare<sup>1</sup>

U. S. Naval Research Laboratory, Washington, D. C.

#### ABSTRACT

Anodic and cathodic polarization curves for the  $\alpha$ -Pd-D system were determined on a palladium bielectrode. The equilibrium potential of the  $(\text{Pd-D})_2/\text{D}^+$  electrode was observed as  $+0.029 \pm 0.001$  v vs. the  $\text{Pt}/\text{D}_2, \text{D}^+$  reference electrode (Stockholm sign convention), in good agreement with the thermodynamic data of Gillespie and Downs (2). The rate constant  $di/d\eta$  of the over-all deuterium-producing reaction on an  $\alpha$ -Pd-D electrode surface in the linear  $\eta$  vs.  $i$  region was found to be about one-half that of the hydrogen-producing reaction on  $\alpha$ -Pd-H. In this region, and at constant overvoltage, the rate of transport of protons through the bielectrode was 1.7 times faster than that of deuterons. It was also found that at low current densities 90% of the deuterium formed on the cathode side migrated through the bielectrode and was ionized on the anode side.

For a  $\beta$ -Pd-D cathode-diaphragm, it was shown that the reaction mechanisms were the same as for a  $\beta$ -Pd-H diaphragm. A calculation was made which showed that at a given atomic concentration gradient the rate of diffusion of hydrogen through a  $\beta$ -Pd diaphragm was  $2\frac{1}{2}$  times faster than that of deuterium.

It was also shown that on a simple  $\beta$ -Pd-D cathode the rate of deuterium production was about one-fourth the rate of hydrogen production on a  $\beta$ -Pd-H cathode. This agrees with the separation factor of 4 found by Farkas (8).

An extensive investigation of the hydrogen-producing reactions on palladium was carried out at this laboratory. These studies have led to a detailed discussion of the mechanisms and thermodynamic

properties of the hydrogen-palladium system. It was felt that a supplementary study of the deuterium-palladium system would provide an interesting comparison and would also add to a more complete understanding of the electrochemical properties of such systems.

<sup>1</sup> Present address: Ford Scientific Laboratory, Ford Motor Company, Dearborn, Michigan.

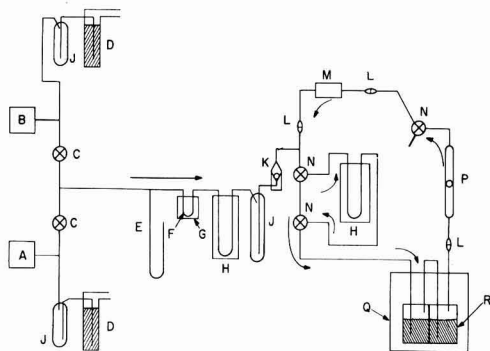


Fig. 1. Gas purification and circulation system: A, deuterium cylinder; B, helium cylinder; C, needle valve; D, mercury safety trap; E, manometer; F, palladium catalyst; G, electric heater; H, liquid nitrogen trap; J, safety trap; K, check valve; L, frittered-glass disc; M, "aquarium type" circulating pump; N, three-way stopcock; P, flowmeter; Q, polyethylene sealed box; R, electrolytic cell.

## Palladium Bielectrode

### Experimental

The experimental technique was the same as that used for the study of the bielectrode in the  $\alpha$ -Pd-H system (1) with the following modifications. In order to conserve deuterium gas a closed system was used as shown in Fig. 1. The deuterium gas was circulated with a specially constructed stainless-steel "aquarium-type" circulating pump. To protect the cell from contaminants and to prevent acid spray from reaching the pump, frittered glass discs were inserted in the inlet and outlet sides of the cell. Further protection was given by placing the pump about 3 ft above the cell.

The deuterium gas and deuterium oxide were obtained from the Stuart Oxygen Company and were better than 99.5% pure. Sulfur trioxide was prepared in an all-glass apparatus by dehydrating fuming sulfuric acid with phosphorus pentoxide (both chemicals were of reagent quality). The sulfur trioxide was distilled and condensed in deute-

rium oxide. In all the following experiments a 2N solution of deuterium sulfate in deuterium oxide was used. A 0.002-in. thick palladium foil was used as the bielectrode. Purified deuterium gas was circulated through the deuterium sulfate solution.

The following procedure was used. Before adding the 2N  $D_2SO_4$  to the rigorously cleaned Teflon cell, the cell and the entire system was thoroughly dried by circulating purified, liquid nitrogen-dried-helium<sup>2</sup> through it for at least 24 hr. Deuterium sulfate solution was then added to only one compartment of the cell. The solution was pre-electrolyzed overnight and the palladium foil was cleaned by anodization under an atmosphere of helium. Deuterium gas was then passed through the system until the helium was flushed out, after which the system was closed and the circulating pump turned on. Small losses of deuterium gas were replaced by manually maintaining a positive pressure of 1 to 2 mm of mercury above atmospheric on the system.

The side of the palladium foil in the compartment containing the deuterium sulfate solution was made a simple anode. The anodic polarization curve was then determined. The average of three runs are shown in Fig. 2.

Deuterium sulfate solution was then added to the second compartment, the solution was pre-electrolyzed overnight and that side of the palladium foil was cleaned by anodization. Both compartments were stirred with deuterium gas until the open-circuit reversible potential of the palladium/deuterium system was reached. This value at  $32^\circ \pm 2^\circ C$  was  $+0.029 \pm 0.001$  v. vs. the Pt/ $D_2$ ,  $D^+$  reference electrode in the same solution (Stockholm sign convention). Overvoltage data were then obtained exactly as before (1). Average results are shown in Fig. 2. The experimental points were reproducible to within  $\pm 2.5$  mv.

### Discussion

The anodic and cathodic polarization curves for the  $\alpha$ -Pd-D system were very similar to those for the  $\alpha$ -Pd-H system. This indicated that the electrode mechanisms were the same as before (1). Gillespie and Downs (2) determined the pressure-concentration isotherms of the deuterium-palladium system, and gave the temperature dependence of the partial pressure  $P$  of deuterium (in atmospheres) at the plateau (two-phase region) as  $\log P_{atm} = 4.633 - 1696.11/T$ . At  $32^\circ C$ , the plateau pressure of deuterium is 0.117 atm.

From the thermodynamic data, the equilibrium potential for the system

$$D^+ + e^- = \frac{1}{2} D_2(0.117 \text{ atm})$$

at  $32^\circ C$  referred to a Pt/ $D_2$ (0.11 atm) electrode in the same solution is  $E = -(RT/2F) \ln 0.117 = 0.028$  v. The equilibrium isotherm of the deuterium-palladium systems at  $32^\circ C$  (Fig. 3) shows that the maximum  $\alpha$ -phase composition is attained at a partial pressure of 0.117 atm. By analogy to the  $\alpha$ -Pd-H system (3), an equilibrium is expected between deu-

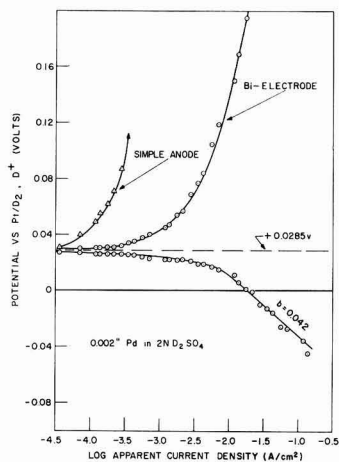


Fig. 2. Overvoltage measurements on the anode and cathode sides of a palladium bielectrode.

<sup>2</sup> For the drying procedure, the liquid nitrogen trap in the circulation loop shown in Fig. 1 was used to dry the cell. During a run, this trap was removed from the system with stopcocks N.

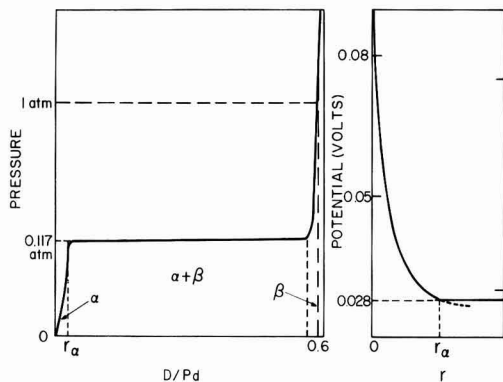


Fig. 3. (left) Phase diagram for the Pd/D<sub>2</sub> system; (right) potential-composition diagram for the Pd/D<sub>2</sub> system ( $r =$  atomic ratio D/Pd).

terium ions in solution and deuterium dissolved in the palladium, independent of the partial pressure of deuterium gas. Here  $D^+ + e^- = (Pd-D)_s$  is the potential determining reaction. The observed reversible potential of  $+0.029$  v for the Pd-D system compared to a Pt/D<sub>2</sub> reference electrode in the same solution saturated with gaseous deuterium at one atmosphere pressure can be considered as the equilibrium potential for this reaction for the maximum deuterium concentration in the  $\alpha$ -Pd-D system. Figure 3 shows the potential vs. D/Pd relationship.

At low current densities there is a linear relation between current density and anodic and cathodic overvoltages (Fig. 4). The slope  $d\eta/di$  for the  $\alpha$ -Pd-D system is twice as large as that for the  $\alpha$ -Pd-H system. The reciprocals of these slopes measure the rate constants of the over-all electrode processes (4). For hydrogen  $di/d\eta$  is 0.143 amp/cm<sup>2</sup> volt while for deuterium it is 0.065 amp/cm<sup>2</sup> volt. This shows that the catalytic activity of  $\alpha$ -palladium for the hydrogen-producing reaction is about twice that for deuterium-producing reactions. The fact that the anodic and cathodic overvoltage for the deuterium forms a continuous linear curve which passes through the point of zero current at 0.0285 v indicates that, as in the case of the hydrogen system, the palladium/deuterium electrode is reversible.

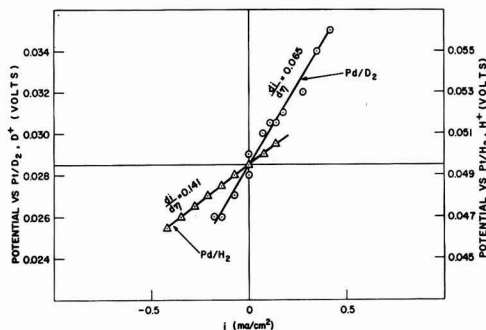


Fig. 4. Comparison of overvoltage vs. current density in the anodic and cathodic low current density region for  $\alpha$ -Pd/D<sub>2</sub> and  $\alpha$ -Pd/H<sub>2</sub> systems in 2N D<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> solutions. Positive currents are anodic, negative, cathodic.

From Fig. 2 a comparison of the simple anode curve with the anode side of the palladium bielectrode in the low current density range can be made. For a given overvoltage a difference in the current density values represents the amount of depolarizing current which flows through the palladium bielectrode. This depolarizing current is a deuteron current density, to be designated by  $j$ , which represents the amount of deuteron current density necessary to reduce the overvoltage of a simple anode to the same value as that found on the anodic side of the bielectrode. A plot of  $j$  vs.  $i$  is given in Fig. 5, where  $i$  is the applied current density on the bielectrode, and obeys the linear relation  $j_D = 0.9i_D$ . For the hydrogen system (1), the same relation is  $j_H = 0.7i_H$ . The difference in the transfer coefficients of the hydrogen and deuterium systems is due to the fact that the rate constant of the hydrogen-producing reaction on the  $\alpha$ -palladium surface is about twice that of the deuterium-producing reaction in the linear  $i$  vs.  $\eta$  range. Since atoms are removed on a palladium bielectrode by surface reaction to form gaseous molecules and by diffusion through the metal to the anode side, and since the surface reaction is slower for deuterium than for hydrogen, then at a given current density, more deuterium diffuses through the metal than does hydrogen. This is shown by the increase in value of the transfer coefficient for deuterium. These results indicate that the magnitude of the transfer coefficient is determined by the rate of the surface reaction.

It is possible to find a set of conditions for 100% transmission of hydrogen or deuterium through a palladium bielectrode. An experiment to show this was carried out as follows. In 2N H<sub>2</sub>SO<sub>4</sub> solutions, bielectrode measurements were made as before, except that the solutions were stirred with helium rather than hydrogen. A simple palladium anode in a helium-stirred solution is completely polarizable, that is, there is no hydrogen oxidation reaction because the partial pressure of this gas is nil and the potential rises as the double layer in the ideally polarized electrode becomes charged to a point where an oxygen or oxide-producing reaction takes place. This can be seen in Fig. 6.

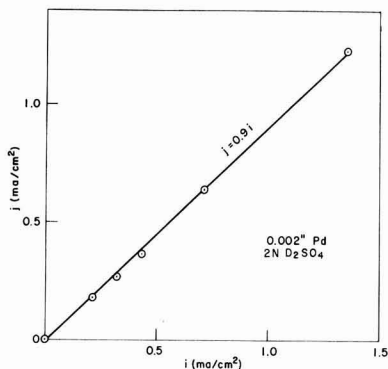


Fig. 5. Relationship between the diffusion current density,  $j$ , and the applied current density,  $i$ , on a palladium bielectrode in 2N D<sub>2</sub>SO<sub>4</sub> solution.

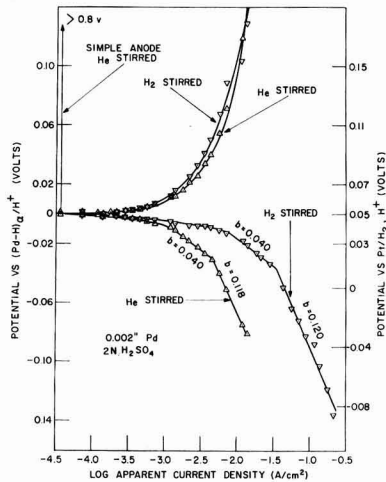


Fig. 6. Effect of replacing  $H_2$  with He stirring on the overvoltage on the anode and cathode sides of a palladium bi-electrode.

Since the anode side of the bi-electrode in helium-stirred solution is not completely polarizable, the oxidation reaction must consist of the ionization of hydrogen atoms. The cathode and anode sides of the bi-electrode being in series demands that all of the atoms formed on the cathode side be transferred to the anode side, otherwise there would be an unbalanced reversible electrode system and part of the oxidation reaction on the anode side would result in the formation of oxide or oxygen with a resulting large increase in the polarization. The fact that at low current densities the anodic branch is the same as that for hydrogen flowing through the cell means that there is a negligible oxygen-producing reaction. Hence it must be concluded that, in the case of helium flow through the compartments,  $j = i$ .

In the low current density range the relations between the depolarizing proton or deuteron current densities and the ratio of their rate constants when  $\eta_D = \eta_H$  can give a measure of the relative transport rates of deuterons and protons. Since  $j_H/j_D = 0.7i_H/0.9i_D$  and  $di_H/di_D = 2.2$  for  $2N H^+$  and  $D^+$  solutions, protons will migrate through Pd 1.7 times faster

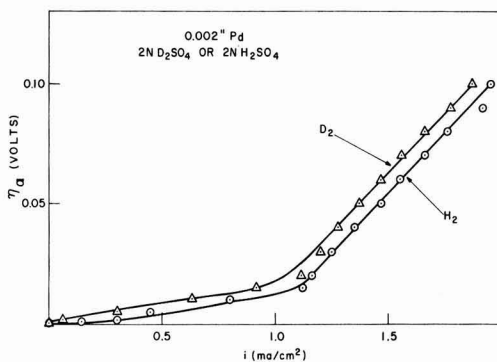


Fig. 7. Comparison of anodic polarization curves of the Pd/ $H_2$ ,  $H^+$  system with the Pd/ $D_2$ ,  $D^+$  system.

than deuterons in these solutions. Under these conditions the polarization on both the anode and cathode sides for both the  $D_2$  and  $H_2$  systems is small and of comparable magnitude. Hence it can be considered that these relative migration rates are essentially per unit of potential gradient.

In a previous paper (1), it was postulated that the rate of transport of hydrogen through the bi-electrode was controlled by the rate of entry (solution) into or exit of hydrogen atoms from the interior of the metal through its skin. It would then follow that in these  $2N$  acid solutions hydrogen dissolves in Pd about 1.7 times faster than deuterium. A comparison of the anodic bi-electrode polarization curves for the H and D systems on the same Pd bi-electrode is shown in Fig. 7. These curves show that the overvoltage at a given current density is always higher for the  $D_2$  system. This is so because the activation energy for the ionization of molecular  $H_2$  is lower.

The cathode branch in Fig. 6 is of interest because it shows that the mechanisms are the same as for the case of hydrogen flow. In addition, it should be noticed that, in comparison to a cathode curve with hydrogen flow, the Tafel,  $b = 0.12$ , slope is reached at a considerably lower current density. This may be explained as follows: In the case of hydrogen flow, hydrogen gas is oxidized to hydrogen ions at the Pt anode, but when the solution is stirred with helium, oxygen is formed at this anode. The oxygen is rapidly transferred to the cathode side of the Pd bi-electrode where it poisons the hydrogen-producing reaction with the result that the 0.12 slope is reached at a relatively low current density. The effect of oxygen poisoning on the change in slope is explained in reference (1). These results support the oxygen poisoning mechanism postulated there.

A few measurements were made in a helium-stirred deuterium sulfate solution which indicated that this system was analogous to the sulfuric acid system.

It should be mentioned that the reversible hydrogen or deuterium reference electrode used in the above helium-flow experiments was one which was independent of hydrogen or deuterium partial pressure. It was shown in this laboratory (3) that the potential-determining reaction on an  $\alpha$ -hydrogen-palladium electrode is  $H^+ + e^- = (Pd-H)_\alpha$ . Similarly it was indicated above that an analogous potential-determining reaction holds in deuterium solutions. Hence a reference electrode can be prepared by placing a palladium wire in hydrogen or deuterium solution and passing their respective gases through the solution until the maximum hydrogen or deuterium concentration in the  $\alpha$ -phase is reached. It has been shown (5) that under these conditions hydrogen will be spontaneously absorbed in the palladium until this maximum  $\alpha$ -phase is reached, at which time the rate of solution of hydrogen in the metal becomes immeasurably slow. These reference electrodes were very suitable for the helium-stirred solutions since they are very stable, reproducible, and are independent of the partial pressure of either hydrogen or deuterium. In addition, they represent the reversible electrode systems for the  $\alpha$ -palladium-

hydrogen or -deuterium electrodes at zero current density. Using these reference electrodes to measure polarization gives the displacement from the reversible condition directly and, hence, the overvoltage of the  $\alpha$ -palladium electrodes.

### Palladium Diaphragm

#### Experimental

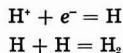
As before (6), the palladium cathode was in the form of a diaphragm separating two isolated bodies of the same solution ( $2N D_2SO_4$ ). The current density-overvoltage relations of the polarization and diffusion sides of the diaphragm were determined with deuterium gas flowing through each compartment of the cell as described above (see Fig. 1).

The experimental technique was the same as reported in reference (6) with the exception that the reference electrodes were Pt/ $D_2$  electrodes in the same solution. The temperature was  $34^\circ C$ . The thickness of the palladium foil was 0.002 in.

The average results of a run in which the current was alternately decreased and then increased for three cycles is given in Fig. 8. The reproducibility of the points was within  $\pm 2$  mv.

#### Discussion

Figure 8 shows that the shape of the polarization,  $\eta_p$ , and the diffusion,  $\eta_d$ , overvoltage vs.  $\log i$  curves was the same as for the corresponding  $\beta$ -Pd-H system. However, since it was postulated (6) that a diffusion mechanism controls the overvoltage on the diffusion side, one would expect that the rate of diffusion of deuterium through the diaphragm should be  $(\frac{1}{2})^{1/2}$  times the hydrogen rate, at equal atomic concentration gradient, since the mass of deuterium is twice that of hydrogen. This was verified as follows: the potentials considered are diffusion overvoltages and no current flows on the diffusion side of the diaphragm; it can therefore be assumed that the concentration of  $H^+$  in the double layer is constant for the potential-determining reactions on the diffusion side. These are



Both steps are virtually at equilibrium and the Nernst potential equation can be used to approximate the activity of hydrogen atoms. Since,

$$E_{Pt} = E^\circ + (RT/F) \ln (H^+)/ (H_2)$$

and

$$E_{Pd} = E^\circ + (RT/F) \ln (H^+)/ (H)$$

then by definition,

$$(\eta_d)_H = E_{Pd} - E_{Pt} = -(RT/F) \ln (H)/ (H_2)$$

and at  $34^\circ C$ ,

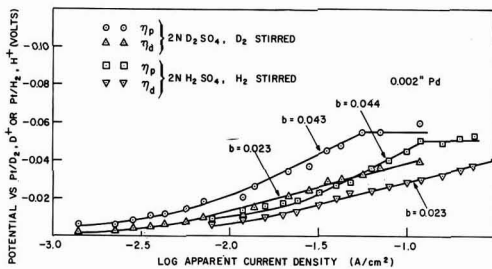


Fig. 8. Hydrogen and deuterium cathodic overvoltage curves on the polarization and diffusion sides of a palladium diaphragm.

$$(\eta_d)_H = -0.060 \log (H)/ (H_2) \quad (I)$$

Similarly for the deuterium-palladium electrode:

$$(\eta_d)_D = -0.060 \log (D)/ (D_2) \quad (II)$$

$(H_2)$  and  $(D_2)$  are the activities of hydrogen and deuterium atoms on the respective platinum reference electrodes;  $(H)$  and  $(D)$  are the activities of these atoms on the diffusion side of the  $\beta$ -palladium diaphragm. Even though no electrolytic current flows on the diffusion side there is an effective atomic diffusion current density through the palladium which causes a polarization of this side of the palladium diaphragm because the concentration of hydrogen or deuterium atoms is a function of the current flow on the polarization side.

At a given current density the  $(\eta_d)_H$  and the  $(\eta_d)_D$  were determined from the curves in Fig. 8. By using relations (I) and (II), the ratio  $(D)/ (D_2) : (H)/ (H_2)$  was determined. This ratio represents the relative rates of deuterium flow to hydrogen flow. If one assumes that the same relation between the atomic diffusion current density,  $\bar{j}$ , and the polarizing current density,  $i$ , found in (6) holds for the deuterium system, then, for a 0.002-in. diaphragm in  $2N D_2SO_4$ :

$$\bar{j}_D = k_D i^{0.58} \quad (III)$$

From (6)  $k_H$  is known and therefore  $\bar{j}_H$  can be calculated. The ratio  $(D)/ (D_2) : (H)/ (H_2)$  multiplied by  $\bar{j}_H$  gives  $\bar{j}_D$ , then  $k_D$  can be found from Eq. (III). Data used for two determinations of  $k_D$  are shown in Table I.

Because of the high concentration of  $H^+$  or  $D^+$  in their  $2N$  solutions, the difference in the polarization and diffusion overvoltages in the Tafel  $b = 0.04$  range essentially represents the concentration gradient of hydrogen or deuterium atoms across the diaphragm. From Fig. 8 the polarization current densities,  $i_H$  and  $i_D$ , can be determined for any given  $\Delta\eta = \eta_p - \eta_d$ . From these polarization current densities,

Table I. Calculation of  $k_D$

$\log i$	$\eta_H$	$\eta_D$	$(H)/ (H_2)$	$(D)/ (D_2)$	$(D)/ (D_2) : (H)/ (H_2)$	$\bar{j}_H$	$\bar{j}_D$	$k_H$	$k_D$
-1.4	-0.019	-0.028	2.073	2.929	1.41	0.0197	0.0278	0.109	0.154
-1.0	-0.0285	-0.0375	2.986	4.217	1.41	0.0321	0.0452	0.109	0.154



Table II. Calculation of  $\bar{j}_H/\bar{j}_D$ 

$\Delta\eta$	$\log i_H$	$\log i_D$	$\bar{j}_H$	$\bar{j}_D$	$\bar{j}_H/\bar{j}_D$
0.018	-0.90	-1.46	0.0363	0.0259	1.40
0.015	-1.04	-1.61	0.0306	0.0216	1.42
0.012	-1.2	-1.76	0.0251	0.0180	1.40
0.010	-1.3	-1.86	0.0223	0.0159	1.40

the atomic diffusion current densities,  $\bar{j}_H$  and  $\bar{j}_D$ , can be determined. These values and their ratio are given in Table II. The ratio  $\bar{j}_H/\bar{j}_D$  is equal to 1.4 for the cases where the concentration gradients of these respective atoms across the diaphragm are the same. This is approximately equal to  $2^{1/2}$ , the value predicted by classical diffusion laws. This result supports the postulate that the overvoltage mechanism on the diffusion side of the diaphragm is controlled by the diffusion of either hydrogen or deuterium atoms, respectively.

It is interesting to note that, as shown in Table I, at a given current density in the Tafel  $b = 0.04$  range, the rate of flow of deuterium across the diaphragm is 1.41 times faster than the rate of flow of hydrogen. This can be explained if the deuterium combination reaction on the polarization side is slower than the hydrogen combination reaction. As a result, for a given current density there will be a larger concentration gradient for deuterium than for hydrogen and consequently the deuterium will flow through the diaphragm at a faster rate. From the experimental data on the bielectrode it is seen that, since the cathodic overvoltage for the deuterium-palladium system is consistently higher than that for the hydrogen-palladium system at the same current densities, the rate of removal of deuterium atoms is appreciably slower than that of hydrogen atoms. This offers supporting evidence for results found on the diaphragm. Additional evidence is given below.

### Simple Palladium Cathode

#### Experimental

In this series of experiments the same clean palladium bead (electrolytically charged to the  $\beta$ -phase) of apparent area  $0.0274 \text{ cm}^2$  was cathodized in pre-electrolyzed  $2N \text{ D}_2\text{SO}_4$  in  $\text{D}_2\text{O}$ ,  $50\% \text{ 2N D}_2\text{SO}_4$  in  $\text{D}_2\text{O} + 50\% \text{ 2N H}_2\text{SO}_4$  in  $\text{H}_2\text{O}$ , and  $2N \text{ H}_2\text{SO}_4$  in  $\text{H}_2\text{O}$ , respectively. During all these runs, a flow of

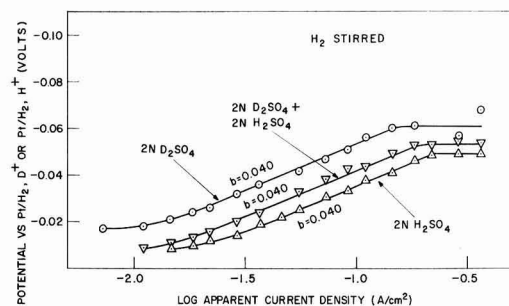


Fig. 9. Hydrogen, deuterium, and a 50-50 mixture overvoltage curve for a simple palladium cathode.

purified hydrogen ( $\text{H}_2$ ) was passed through the cell. Within our experimental time limits ( $<24 \text{ hr}$ ) the exchange between  $\text{H}_2$  and  $\text{D}^+$  is negligible because of the relatively small area of exposed metal surface. The reference electrode was always a platinum electrode in the same solution. The temperature was  $30^\circ \pm 2^\circ \text{C}$ . The experimental details were the same as those described in earlier work (7). The cathodic overvoltage curves obtained are shown in Fig. 9. Figure 10 shows the overvoltage vs.  $i$  relationship at low current densities. In all cases the palladium bead was electrolytically charged with hydrogen or deuterium to the  $\beta$ -phase before overvoltage measurements were taken.

#### Discussion

The curves in Fig. 9 indicate that the mechanisms for the deuterium-producing reactions are the same as those described for hydrogen (7). As hydrogen ion is replaced with deuterium ion the exchange current,  $i_0$ , for the  $b = 0.04$  range, is decreased and the value of the overvoltage plateau increases. Figure 10 shows that as the deuterium concentration is increased the rate constant,  $-di/d\eta$ , decreases in about a linear fashion. The ratio of the rate constants for pure  $\text{H}^+$  compared to pure  $\text{D}^+$  is about 4:1 which gives a separation factor consistent with that found by other investigators (8). All of these results confirm the findings above that the catalytic activity of palladium for hydrogen-producing reactions is greater than for deuterium-producing reactions.

These results contradict the conclusion of Farkas (8) that the rate of the removal of deuterium atoms from the palladium cathode is faster than the removal of hydrogen atoms to form molecules. His conclusion may be considered to be in error for the following reasons. Farkas assumed that the removal of atoms from the palladium surface was by combination, whereas our work has shown that removal is normally both by combination and electrochemical desorption. In strong acid solutions, electrochemical desorption predominates. His experimental results are actually consistent with our findings. If hydrogen is generated four times faster than deuterium on the cathode (as shown in Fig. 10) and if it dissolves in palladium 1.7 times faster than deuterium (as shown above), then the ratio  $\text{H}/\text{D}$  dis-

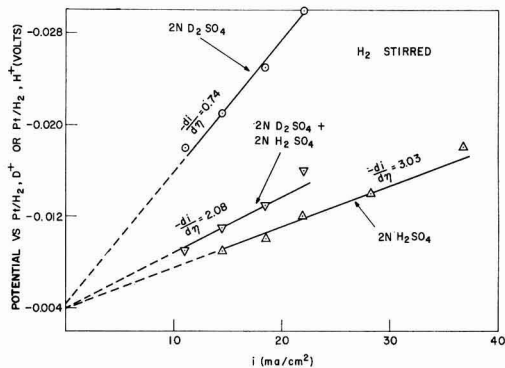


Fig. 10. Comparison of the relative rates of the hydrogen- and deuterium-producing reactions at a  $\beta$ -palladium cathode.

solved in the Pd is about 6.8. This compares favorably with the experimental value of 6.6 found by Farkas.

### Conclusions

1. The electrochemical mechanisms of deuterium-producing reactions on Pd are the same as those of the hydrogen-producing reactions on Pd. This statement holds true for the cases where the Pd was investigated as a bielectrode, as a cathode diaphragm, or as a simple cathode.

2. In all cases it is found that the catalytic activity of Pd is greater for H<sub>2</sub>-producing reactions than for D<sub>2</sub>-producing reactions.

3. It was found that: (a) in the linear  $\eta$  vs.  $i$  range H<sub>2</sub> is produced at an  $\alpha$ -Pd cathode about twice as fast as D<sub>2</sub>; (b) in 2N acid solutions hydrogen ions are transferred through a Pd bielectrode 1.7 times faster than deuterium ions in the very low current density range; (c) in the linear  $\eta$  vs.  $i$  range H<sub>2</sub> is produced at a  $\beta$ -Pd cathode about 4 times faster than D<sub>2</sub>; (d) for a given polarizing current density, H diffuses (in the Tafel  $b = 0.04$  region) through a Pd diaphragm 1.41 times slower than D (because of item 2 above); (e) For a given value of  $\Delta\eta = \eta_p - \eta_c$  (same atomic concentration gradient across diaphragm) H diffuses through a Pd diaphragm 2½ times faster than D.

4. An  $\alpha$ -Pd electrode is a stable and acceptable reversible atomic hydrogen reference electrode for systems in which H<sub>2</sub> or D<sub>2</sub> gas is not available and in which oxidizing agents are absent.

### Acknowledgments

The authors are indebted to Dr. J. C. White for many helpful discussions. They also wish to thank Professor R. A. Marcus of the Brooklyn Polytechnic Institute for his valuable comments.

Manuscript received Feb. 26, 1957. This paper was prepared for presentation before the New York Meeting, April 27-May 1, 1958.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1958 JOURNAL.

### REFERENCES

1. J. P. Hoare and S. Schuldiner, *This Journal*, **104**, 564 (1957).
2. L. J. Gillespie and W. R. Downs, *J. Am. Chem. Soc.*, **61**, 2496 (1939).
3. S. Schuldiner, G. W. Castellan, and J. P. Hoare, *J. Chem. Phys.*, **28**, 16 (1958).
4. P. Dolin, B. Ershler, and A. Frumkin, *Acta Physicochim. USSR*, **13**, 782 (1940).
5. J. P. Hoare, S. Schuldiner, and G. W. Castellan, *J. Chem. Phys.*, **28**, 22 (1958).
6. J. P. Hoare and S. Schuldiner, *This Journal*, **103**, 237 (1956).
7. J. P. Hoare and S. Schuldiner, *ibid.*, **102**, 485 (1955).
8. A. Farkas, *Trans. Faraday Soc.*, **33**, 552 (1937).

## Uncommon Valency Ions and the Difference Effect

M. E. Straumanis

Department of Metallurgy, University of Missouri School of Mines and Metallurgy,

Rolla, Missouri

### ABSTRACT

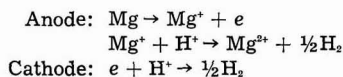
It is shown that in evaluating the rates of anodic dissolution processes it is necessary to consider the influence of the positive and negative difference effects; otherwise ions going into solution with uncommon valency may be found. Scale fragments detached from an aluminum anode by the current passing through it could be seen. The hypothesis of valence change of ions while a current is passing through the anode does not explain all observed facts, but they can be well explained by the theory developed for the positive and negative difference effects.

It has been found not only in the past but also recently that in certain anodic processes ions with an uncommon valency went into solution. For instance, the formation of monovalent Mg ions, which subsequently reacted with water under hydrogen evolution, has been discussed (1-3). Occasionally an increase of the charge of ions going anodically into solution could also be calculated.

To study the anodic dissolution phenomena and the valency of ions formed anodically, a very simple device can be used (Fig. 1). The driving force of the cell is provided by the anodic metal itself. In the case of a Mg or Al anode one easily can observe that, on closing the switch of the circuit, hydrogen evolution starts not only at the Pt cathode, but also at the anode (or the rate of evolution increases at the anode). If the current is then turned off, H<sub>2</sub>

evolution ceases, or decreases strongly, at both electrodes. However, quantitative measurements show that the total amount of H<sub>2</sub> developed and the weight loss of the anode is larger than that calculated from the current by Faraday's law. It was concluded from this that the anodic metal went into solution with lower valency (1-4).

Two explanations have been proposed for this effect: (a) the lower or changed valency hypothesis, which explains the simultaneous H<sub>2</sub> development on the cathode and anode, for instance in case of Mg:



but does not explain the larger total amount of H<sub>2</sub>

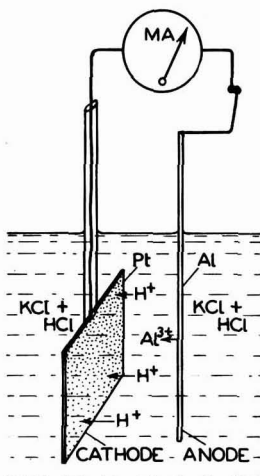


Fig. 1. Device to observe the negative and positive  $\Delta$  effects

developed; (b) the difference ( $\Delta$ ) effect theory explains all the phenomena observed (5-8) and besides the development of hydrogen in addition to that produced by the current flowing through the cell, Fig. 1. Unfortunately, the  $\Delta$ -effect was not taken into consideration by the previous investigators (1-4) and formation of lower valency ions was assumed.

According to the theory of the negative  $\Delta$ -effect (8) the very active metals (Mg, Al, Ti) react with the electrolyte (self-dissolution) in places where the protective scale is broken off from their surface. The scale can be spalled off the metal, more or less completely by passing an anodic current through the surface of the metal. If this current is interrupted the scale regenerates more or less slowly and rate of self-dissolution reduces or even ceases. All the phenomena observed are explained by this mechanism including the reducing power of the anolyte (9) during passage of the current. In case of Mg reaction in a KCl solution, the external current produces the soluble and the self-dissolution reaction (on the stripped areas of the metal) the insoluble reaction products. As the extension of these areas is roughly proportional to the anodic current (9), the ratio of the insoluble and of the soluble products is nearly constant. Occasionally, depending on the purity of the Mg, this ratio may approach 1:1, a possibility overlooked by Tomashov (10).

However, the stripping of the scale by the passing anodic current needs some additional evidence. The appearance of scale fragments can easily be observed by a device shown in Fig. 1, if, as anodic metal, an Al wire and, as an electrolyte, KCl (about 100 g/l) dissolved in an about 0.1N HCl solution are used. Observing the wire through a magnifying glass, nearly no development of hydrogen (with the switch open) can be seen (Fig. 2). Upon closing the switch the rate of self-dissolution of the wire clearly increases and fragments of the scale are torn off by the anions going into solution and carried up by the hydrogen bubbles (Fig. 2B). The fragments at that stage are not observable directly.

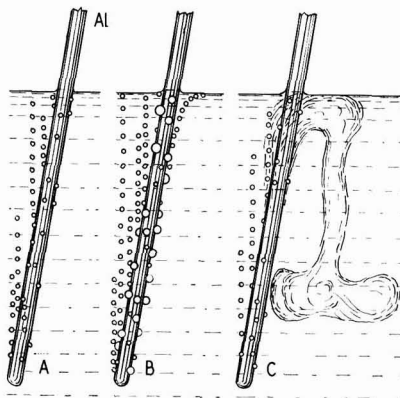


Fig. 2A. Aluminum wire as an anode in a KCl-HCl solution with the switch (Fig. 1) open. Fig. 2B. The self-dissolution of the Al wire increases with the switch closed. Fig. 2C. After interruption of the current,  $H_2$  evolution decreases and a cloud of white dust, sinking down, appears.

However, they can be noticed as soon as the current is interrupted and the intense hydrogen evolution decreases. The particles now sink down in the form of a cloud of whitish dust (Fig. 2C). The sinking cloud can be observed best when the wire is tilted. Very small hydrogen evolving metallic particles can also be seen floating in the electrolyte, which evidently were separated from the wire together with the scale. The white particles cannot be  $Al(OH)_3$  formed later ( $Al^{3+} + 3 OH^-$ ), because the solution was strongly acidic the entire time. Thus, the particles could originate only from the scale which is difficultly soluble in diluted HCl. No such dust clouds could be observed in a solution of HF, evidently because the scale is easy soluble in this acid.

If these arguments are not regarded as being strong enough to disprove the lower valency theory, then there is also a reverse phenomenon, the positive  $\Delta$ -effect (8-11). Using HF (~0.1N) instead of the KCl-HCl mixture one will observe a sudden decrease in the rate of dissolution ( $\Delta$ -effect) of the Al wire as soon as the circuit (Fig. 1) is closed. However, after interruption of the current, the previous rate will be restored. Having subtracted this self-dissolution rate from the total rate obtained with the current on, one nevertheless will find that less Al went into solution as calculated from the current. This effect of sudden decrease in rate can never be explained by the presence of oxygen in and above the acid. So, disregarding the positive  $\Delta$ -effect, one has to postulate the formation of Al ions with a valency higher than 3. While Mg or Al ions with a valency lower than the normal are still possible, the formation of ions of higher valency in aqueous solutions is theoretically unreasonable (12). Besides, why, during the passage of an anodic current, should  $Al^+$  or  $Al^{2+}$  be formed in HCl solutions and  $Al^{4+}$  in HF solutions? Ions of uncommon valency [sometimes even lower than one (9)] will always be found in anodic dissolution processes, if the  $\Delta$  effects influencing the self-dissolution rates are disregarded. Besides, the fact that the effects are

functions of current density has always to be considered. If, after all the corrections for the rates are made, some positive or negative rate being outside the limits of error still remains, this may be attributed to the appearance of ions of uncommon valency.

Manuscript received April 8, 1957. This paper was prepared for delivery before the Washington Meeting, May 12-16, 1957.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1958 JOURNAL.

#### REFERENCES

1. R. L. Petty, A. W. Davidson, and J. Kleinberg, *J. Am. Chem. Soc.*, **76**, 363 (1954).
2. J. H. Greenblatt, *This Journal*, **103**, 539 (1956).
3. E. H. Phelps, Electrochem. Soc. Cleveland Meeting, Abstr. 61 (1956).
4. P. Brouillet, G. Epelboin, and M. Froment, *C.R.*, **239**, 1795 (1954).
5. A. Thiel and J. Eckell, *Z. Elektrochem.*, **33**, 370 (1927).
6. M. A. Streicher, *J. (and Trans.) Electrochem. Soc.*, **93**, 304 (1948).
7. W. O. Kroenig and V. N. Uspenskaja, *Korrosion u. Metallschutz*, **11**, 10 (1935); **12**, 123 (1936).
8. M. E. Straumanis and Y. N. Wang, *This Journal*, **102**, 304 (1956).
9. M. D. Rausch, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, **77**, 2093 (1954).
10. N. D. Tomashov, V. S. Komissarova, and M. A. Timinova, *Tr. Fiz. Khim. Inst. Akad. Nauk, USSR*, **4**, 172 (1955).
11. M. E. Straumanis and P. C. Chen, *This Journal*, **98**, 351 (1951).
12. See also, E. Lange in H. Fischer, K. Hauffe, and W. Wiederholt, "Passivierende Filme und Deckschichten," pp. 385, 387, Springer-Verlag, Berlin (1956).

## Technical Note



### A Technique for Purifying Electrolytic Solutions

D. A. Vermilyea

Research Laboratory, General Electric Company, Schenectady, New York

One of the most difficult problems which arises in studies of surface reactions in solutions is that of contamination by adsorbed impurities. Vahramian (1) suggested a method for rendering ineffective the impurities responsible for the passivation<sup>1</sup> of silver electrodes in nitrate solutions, and it may be that the same method is applicable in other situations. It therefore seemed worthwhile to verify the

<sup>1</sup>Passivation means prevention of growth or solution of a crystal exposed to a supersaturated or undersaturated medium.

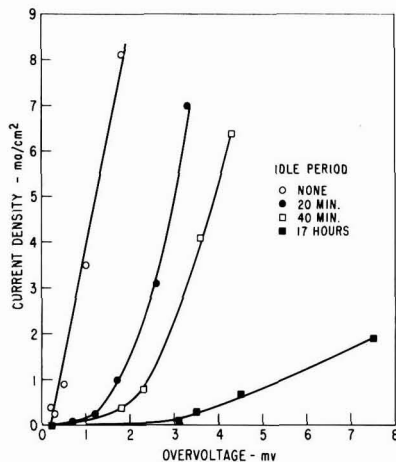


Fig. 1. Electrodeposition from nonoxidized solution

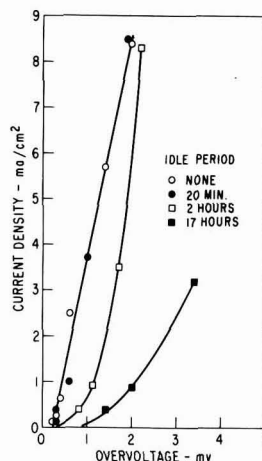


Fig. 2. Electrodeposition from oxidized solution

method and to call it to the attention of people studying crystal growth and electrode reactions in solutions.

The suggestion was that the impurities responsible for the passivation of silver electrodes in silver nitrate solutions could be oxidized by bubbling oxygen through the solutions for 24 hr in the presence of platinumized platinum. The temperature recommended by Vahramian was 60°C; the writer has obtained equally good results at 60° and 100°C. Figures 1 and 2 show current voltage curves for

silver electrodes allowed to remain idle for various periods of time in  $N AgNO_3$  solutions before and after "oxidation" as suggested by Vahramian. While an idle period of 1 or 2 min resulted in serious passivation in the solution before oxidation, it was possible to leave electrodes idle for periods of at least 30 min in the solution after oxidation without noticeable contamination. Even the electrode left overnight was not as badly contaminated as the one left 20 min in the solution as prepared. The method thus works very well indeed.

This writer has also found that very strong oxidizing treatments, such as boiling the solution after adding  $KMnO_4$  or  $K_2S_2O_8$ , eliminated passivation. These other treatments had undesirable results such as the formation of a precipitate or the formation of divalent silver, and introduced unwanted ions into the bath. For this reason the simple oxidation with oxygen is preferable. Activated alumina and acti-

vated charcoal were also tried, both with and without oxygenation, but these treatments did not eliminate passivation. Also, when oxygen free nitrogen or helium (instead of oxygen) was used as the atmosphere in the cell while the solution was heated in contact with platinized platinum passivation was not eliminated. It thus appears that either oxygen plus a catalytic surface or a very strongly oxidizing condition is required to eliminate passivation. It seems likely that the explanation given by Vahramian—that passivation is eliminated in "oxidized" solutions because of the oxidation of organic impurities—is correct.

Manuscript received Dec. 23, 1957.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1958 JOURNAL.

#### REFERENCE

1. A. T. Vahramian, *Acta Physicochim.*, **19**, 148 (1944).



# FUTURE MEETINGS OF The Electrochemical Society



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

Headquarters at the Chateau Laurier

Sessions probably will be scheduled on

Batteries, Corrosion, Electrodeposition (including symposia on "Electrodeposition on Uncommon Metals" and "Chemical and Electropolishing"),

Electronics (Semiconductors), Electro-Organics,

Electrothermics and Metallurgy,

and a symposium on "Films Formed in Contact with Liquids"

sponsored by Theoretical Electrochemistry, Battery, and Corrosion Divisions

★ ★ ★

**Philadelphia, Pa., May 3, 4, 5, 6, and 7, 1959**

Headquarters at the Sheraton Hotel

★ ★ ★

**Columbus, Ohio, October 18, 19, 20, 21, and 22, 1959**

Headquarters at the Deshler-Hilton Hotel

★ ★ ★

**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 Ottawa, Canada, September 28-October 2, 1958. Triplicate copies of each abstract (*not exceeding 75 words in length*) are due at the Secretary's Office, 1860 Broadway, New York 23, N. Y., *not later than June 2, 1958* in order to be included in the program. *Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at 1860 Broadway, New York 23, N. Y.

**DELCO RADIO,**

*developers and producers of high power transistors, offers*

# CHALLENGING JOB OPPORTUNITIES

*for experienced*

**PHYSICISTS** . . . to work on semiconductor device design and development, materials research, fabrication processes, and materials preparation.

**CHEMISTS** . . . to work on etching and electroplating problems, materials preparation, diffusion and alloy studies, surface studies, and other problems associated with semiconductors and semiconductor devices.

**ELECTRICAL ENGINEERS** . . . to work on transistor applications, field engineering, and product design and development.

*Act Now!* Join the company that's unique in the electronics industry: We engineer and manufacture most of the wide variety of parts used in our products! What's more, we have enjoyed twenty-two years of engineering and manufacturing leadership. Positions are permanent, offer excellent growth potential and G.M. employe benefits. Living is pleasant in small engineer's community. Also, the opportunity is yours to do advanced degree work that is company supported.

*Send résumé to Mr. C. D. Longshore, Salaried Employment Supervisor, Dept. G.*



**DELCO RADIO**

*Division of General Motors, Kokomo, Indiana*



## Highlights of the Board of Directors' Meeting

(Held January 24, 1958, Hotel Statler, New York, N. Y.)

The minutes of the last meeting were approved as distributed.

President Hackerman declared that the new Constitution had been approved and that it and the new Bylaws would become operative at the time of the Spring 1958 convention. The President declared that Sherlock Swann, Jr., had been elected President for the forthcoming year, and Henry B. Linford Vice-President, to take office at 8:00 A.M. on the last day of the Spring 1958 convention. L. I. Gilbertson was re-elected Treasurer.

Upon the President's announcement that Henry B. Linford (currently Secretary) will be third Vice-President as of 8:00 A.M. on the last day of the Spring 1958 Meeting, the Board voted that the President-Elect shall recommend, for the approval of the Board of Directors, an interim Secretary to take office at 8:00 A.M., Thursday, May 1, 1958, and to serve until his elected successor takes office.

W. J. Hamer was appointed to represent the Society at the initial meeting of the Advisory Board on Critical Tables to be held February 3, 1958, and Ernest Yeager was named our representative at the Conference on a National Center for Coordination of the World's Science Information to be held at Western Reserve University on February 3 and 4, 1958.

The Board approved the President's appointment of A. L. Ferguson and H. A. Liebhafsky to the Palladium Medal Committee, replacing Norman Hackerman and J. P. Fugassi, their terms to begin on May 1, 1958.

The Treasurer reported that at this time we have an excess income over expenses of \$5,500.00; therefore, we can expect to stay well in the black for the rest of this fiscal year. The proposed budget for the fiscal year April 1, 1958-March 31, 1959 was approved and is published here in its entirety. Several minor changes over previous budgets have been made—Publication Committee expense will be included in the Printing and Mailing of the JOURNAL expense in the future; Advertising expense has been removed since our agency is no

longer active; an Officer Travel Fund has been established; and New Capital Equipment has replaced Reserve for New Office Equipment and will be used to purchase new office equipment for the national office.

The Bylaws for the Indianapolis, Columbus, and Southern California-Nevada Sections were approved, along with the revised Corrosion Division Bylaws.

The Board expressed its appreciation to R. B. MacMullin for his exceptionally comprehensive report of the Buffalo Meeting. This report will be distributed to other local committees in the future since it contains information that will be of great assistance in the handling of future meetings.

The Executive Secretary (currently designated Assistant Secretary) was given approval to attend the meeting of the Council of Engineering Society Secretaries to be held during May 1958 in Cleveland.

At the request of the Secretary, the Board agreed that the Asia Foundation should be contacted in order to secure the Foundation's continued financial support of our India Section members to the extent of \$5.00 per member.

F. A. Lowenheim requested closer cooperation with the Division chairmen and chairmen of symposia in estimating attendance at technical sessions so that the local committee may provide adequate meeting facilities. This estimate of attendance is necessary, preferably a year in advance.

John Convey reported that a trip to the Atomic Energy Plant at Chalk River is being planned for the Ottawa Convention. Tentatively, this trip would be made on the Friday following the technical sessions.

The Board approved a motion made by R. A. Schaefer to return the previous Columbus Convention Fund, amounting to \$400.00, to Columbus, now constituted as the Columbus Section.

W. C. Gardiner, Chairman of the Ways and Means Committee, reported that at Buffalo the Board ap-

proved the policy of photographing of slides and the making of recordings at technical sessions as part of the Instructions to Chairmen of Technical Sessions. Since recordings have never been sanctioned by the Board, it was voted that slides may be photographed at technical sessions of the Society provided that such action is acceptable to the speaker and the Chairman of the session, and that the taking of sound recordings at technical sessions at meetings is contrary to the policy of the Society. By this action the Buffalo decision of the Board was revised.

Dr. Gardiner read a statement of policy, which was prepared by the Ways and Means Committee after consideration of a problem discussed in a letter from Herbert Bandes to the President regarding broadening the scope of interest of the Society, which was approved by the Board:

"The Ways and Means Committee is of the opinion that the best interests of the Society can be served within the (present) framework of interests and objectives of its Divisions. It is the privilege and duty of the Divisions to organize symposia that are of interest to their members. The Divisions are urged to promote membership in the Society by their own efforts through their representatives on the Membership Committee. It is the understanding of the Ways and Means Committee that the Publication Committee is ready and willing to cooperate with any Division wishing to publish material that is outside of the editorial policy of the JOURNAL."

On the recommendation of the Ways and Means Committee, it was voted that the Formal Opening ceremony of the convention be left to the discretion of the local committee and the President.

The Board approved the recommendation of the Finance Committee to re-establish the Corrosion Handbook Fund as a general item in the portfolio.

It was voted that the Board shall fix the Executive Secretary's salary; all others, with the exception of the

Managing Editor's, will be adjusted at the discretion of the Executive Secretary, who shall act as the Society's Office Manager.

Two requests for microfilming and reprinting out-of-print issues of the JOURNAL were presented by R. J. McKay, Chairman of the Publication Committee; after considerable discussion this was referred back to the Publication Committee for further study since the Society already has an agreement on this with another company.

JOURNAL statistics presented by the Editor show that the hold-up of papers in review is still a major problem and the chief cause of delay in publication.

M. F. Quaely, proxy for F. W. Koerker, presented the report of the Membership Committee in which current total membership is listed as 2,735. The number of members representing Sustaining Members increased to 70 and those representing Patron Members remained the same at 8. The Membership Committee

recommended that a record should be kept of new memberships and net membership changes. There was an increase of 347 Active Members; however, changes in Life, Emeritus, Associate, Student, and Honorary membership changed the net to 335 increase. The increase during the past eight years is as follows: 1950—27, 1951—64, 1952—81, 1953—51, 1954—52, 1955—129, 1956—249, 1957—335.

Hans Thurnauer's report of the Sustaining Membership Committee was read by the Secretary. It was noted that since the Buffalo Convention, the response to 65 letters written to companies who had sent members or guests to our meeting was very gratifying, and resulted in seven new Sustaining Members. The Olin-Mathieson Chemical Corp. has become the fifth Patron Member of the Society.

President Hackerman reported that he had recently completed a tour of new Sections of the Society—Indianapolis, Columbus, and Mohawk-Hudson—and hoped to tour all of the continental Sections of the Society before the end of his term of office.

Robert K. Shannon,  
Assistant Secretary

Proposed Budget, 4/1/58-3/31/59

Income

	Final budget 1957-58	Proposed budget 1958-59
All Membership Dues .....	\$ 39,200	\$ 43,480
Patron & Sustaining Membership		
Dues .....	16,000	17,000
Reprints .....	4,700	10,000
Nonmember Journal Subscriptions..	22,000	27,450
Office Sale Journal & Publications...	500	500
Advertising .....	12,500	9,000
Bound Volumes .....	2,500	2,500
Conventions .....	5,300	5,000
	<u>\$102,700</u>	<u>\$114,930</u>
<i>Society Reserve Fund:</i>		
Nonmember Journal Subscriptions	4,200	5,490
Nonmember Convention		
Registrations .....	2,520	2,500
Monograph Royalties .....	6,000	3,500
Income from Investments .....	1,800	2,000
	<u>\$ 14,520</u>	<u>\$ 13,490</u>
Total .....	<u>\$117,220</u>	<u>\$128,420</u>

Expenses

Printing and Mailing Journal .....	\$ 40,000	\$ 40,000
Reprints .....	2,500	7,000
Advertising .....	5,200	—
Publication Committee .....	350	—
Salaries .....	44,500	47,000
Rent .....	4,000	3,600
Postage, Supplies, Miscellaneous		
Expense .....	6,200	6,500
Local Sections & Divisions .....	1,000	1,500
Young Author's Prize .....	100	100
New Capital Equipment .....	585	600
Bound Volumes .....	3,000	3,000
Officer Travel Fund .....	—	1,000
New York Office Travel .....	1,400	1,400
Meeting Expenses:		
Program Booklets .....	1,500	2,000
Materials, Supplies, Postage, & Express .....	820	1,000
	<u>\$111,235</u>	<u>\$114,700</u>
Contingency—1% of Estimated Income .....	1,027	1,150
Total .....	<u>\$112,262</u>	<u>\$115,850</u>
Excess Expenses Over Income,		
General Fund .....	\$-9,562	\$ -920
Income Credited to Society Reserve Fund .....	+14,520	+13,490
Net Excess Income Over Expenses..	<u>\$+4,958</u>	<u>\$+12,570</u>

## Section News

### Boston Section

The eleventh meeting of the Boston Section, on March 5, was a joint meeting with the Greater Boston Section of the National Association of Corrosion Engineers. Dr. Harry C. Gatos, of M.I.T.'s Lincoln Lab., spoke on "The Corrosion of Germanium," summarizing especially the recent work of his group. The solubility of germanium in water with dissolved oxygen, and in oxygen-free water with hydrofluoric or nitric acid was investigated, and the effects of surface treatments, crystallographic orientation, and concentration of mobile carriers were determined. Conditions when passivation occurs were also established.

The report of the Nominating Committee (Chairman, Herbert Bandes) for Section Officers for 1958-59 was read. The Committee also recommended that a change be made in the Bylaws so as to separate the positions of Secretary and Treasurer.

The next meeting is planned for May 12, with Dr. Herbert Bandes speaking on "Chemistry in the Electronics Industry."

Worden Waring,  
Secretary-Treasurer

### Mohawk-Hudson Section

The sixth meeting of the Mohawk-Hudson Section of the Society was held at the Edison Club at Rexford, N. Y., on January 22.

The Section was fortunate to be able to present as its speaker of the evening Dr. Norman Hackerman, President of The Electrochemical Society and chairman of the Dept. of Chemistry of the University of Texas. Dr. Hackerman chose as the subject for his lecture "The Passivity of Metals."

The seventh meeting of the Section was held at 8:00 P.M. on Tuesday, February 4, at the Edison Club, Rexford, N. Y. This was a joint meeting with the National Association of Corrosion Engineers, and in view of this fact the usual business session of the meeting was omitted.

The speaker of the evening was Dr. E. N. Skinner of the International Nickel Co., who spoke on the subject of "High Temperature Corrosion."

A. L. Jenny,  
*Secretary-Treasurer*

### Ontario-Quebec Section

The second meeting of the Section to be held in Toronto, Ont., took place Friday afternoon, January 24, at the University of Toronto. T. S. Gamble, Section Chairman, turned the meeting over to Dr. G. E. Willey, Technical Chairman, who introduced the guest speakers: Mr. R. Smallman-Tew, chief metallurgist at AVRO Aircraft Ltd., Toronto, and Dr. L. M. Pidgeon, head of the Dept. of Metallurgical Engineering at the University of Toronto.

Two most interesting and informative talks were presented dealing with development and production of metals and alloys required in the aircraft industry. Mr. Smallman-Tew discussed the properties necessary in materials for future planes flying at supersonic speeds, and showed a number of slides depicting the relation between tensile strength and temperature for various metals and alloys. Dr. Pidgeon covered the present position and future trends in the production of steel, aluminum, magnesium, and titanium, and indicated that, without government or other subsidy, development of new and improved materials for aircraft manufacture will be slow because the demands are exacting and the market is relatively small.

The third meeting of the Ontario-Quebec Section for the 1957-58 season was held at McGill University in Montreal, Friday afternoon, February 28. Under the chairmanship of T. S. Gamble a short business meeting was held first, at which a report of the

Nominating Committee proposing candidates for office in the Section for the 1958-59 term was received. The slate of officers as proposed and as shown below was elected, as there were no further nominations from the floor:

*Honorary Chairman*—John Convey  
*Chairman*—R. R. Rogers

*Vice-Chairman (Program)*—H. A. Timm

*Vice-Chairman (Membership)*—L. G. Henry

*Secretary-Treasurer*—Jack Noy  
*Executive Committee*—T. S. Gamble, R. P. Bailey, John Ogilvie, A. E. Edwards

Following the business meeting, Mr. H. W. Umphrey, Technical Chairman, introduced the guest speakers, Dr. Vittorio de Nora of the firm of Oronzio de Nora, Impianti Elettrochimici, Milan, and Dr. R. D. Lynch, senior design engineer, Semi-Conductor Div., Westinghouse Electric Corp., Youngwood, Pa. Dr. de Nora gave a most interesting talk on modern mercury cells for manufacture of chlorine and caustic soda, discussing the general principles of mercury cell operation, recent developments in horizontal cells, and possible future vertical cathode cells. Dr. Lynch discussed the history and development of semiconductors, their application in the electrochemical and other fields, and the characteristics and special features of silicon rectifiers.

L. G. Henry,  
*Secretary-Treasurer*

### Philadelphia Section

Norman Hackerman, National President of The Electrochemical Society, was the speaker at the March 5 meeting of the Section at the Harrison Lab. of Chemistry, University of Pennsylvania.

Dr. Hackerman, who is internationally known for his productive research in the physics and chemistry of surfaces, presented a new theory of passivity based on adsorption of ions on top of a passivating layer. In this way it is possible to explain the fact that under special circumstances only extremely small amounts of electricity (e.g., 45 microcoulombs/cm<sup>2</sup>) are required to produce passivity, or, in other words, a major change in electrode potential. The ionic species adsorbed on top of a passivating oxide layer can be oxygen or hydroxyl ions.

The Section was honored by the presence of Dr. H. Gerischer of the Max Planck Institute in Stuttgart, Germany. Both Dr. Hackerman and Dr. Gerischer visited the Research

Dept. of the Electric Storage Battery Co. in Philadelphia.

The next meeting of the Philadelphia Section will be held at the RCA Labs. in Princeton on May 17.

Paul Ruetschi

### Washington-Baltimore Section

The third regular meeting of the 1957-58 year was held on December 5, 1957 at the National Bureau of Standards. The speaker was Dr. Karl Sollner of the National Institute of Health and his topic was "Some Recent Work in the Physical Chemistry of Membranes." He discussed work done in his laboratory during the past few years, as well as some of the recent technological developments. One objective in the laboratory is to find membranes with high selectivity for anions or cations and with low resistance. Resistance determines the rate of exchange of ions across membranes. With membranes, it is possible to accumulate electrolyte against a concentration gradient up to 85%. At this point small imperfections in the membrane cause enough leakage to prevent further concentration. This work may help explain the mechanism by which the concentrations of electrolytes in living cells become higher than in the surroundings. Membranes will eventually be used to de-salt water in large quantities.

The fourth regular meeting of the 1957-58 year was held on January 2, 1958 at the National Bureau of Standards. The program included talks by Mr. William W. Gullet of the Chicago Development Corp. and Dr. John W. Kallander of the Naval Research Lab.

Mr. Gullet spoke on "Recent Developments in the Electrowinning of Titanium." He described the process which utilizes a fused sodium chloride bath containing approximately 5% titanium. Two 10,000-amp cells are now in operation. Soluble anodes made of ferrotitanium containing 90% titanium can now be used in this process. Titanium containing less than 0.02% oxygen may be produced with the fused chloride process. Metal of this purity makes alloys with radically new properties a possibility.

Dr. Kallander's topic was "Problems Involved in Dielectric Measurements During Irradiation." His work is part of a program to determine the physical and chemical effects of the degradation of insulation under various stresses. Results obtained using 0.4 megarontgens per hour with 60 cycle a-c and d-c currents show that irradiation does not affect the electric strength significantly.

David Schlain, *Secretary*



---

## Division News

---

### Fall 1958 Symposium on "Films Formed in Contact with Liquids"

A symposium on "Films Formed in Contact with Liquids" under the sponsorship of the Theoretical Electrochemistry, Battery, and Corrosion Divisions is planned for the Fall 1958 Meeting of the Society to be held in Ottawa, Canada, September 28-October 2, 1958.

Triplicate copies (not exceeding 75 words in length) must reach the Secretary's Office, 1860 Broadway, New York 23, N. Y., not later than June 2, 1958 in order to be included in the program. Indicate on abstract that the paper is intended for this symposium.

---

## Personals

---

**Roy G. Post**, formerly of Richland, Wash., recently took a position with Texas Instruments, Inc., Operations Research Section, Semiconductor Components Div., Dallas, Texas.

**C. Bruce Brown** has joined St. Paul Ammonia Products Inc., South St. Paul, Minn. He had been with Campbell & Associates Reg. in Montreal, Canada.

**John R. Smyth**, former chief control engineer, has been named to the newly created post of assistant director of engineering at Exide Industrial Div., Electric Storage Battery Co., Philadelphia, Pa. He continues to supervise all material and process control engineering and, in addition, now has line authority for all battery engineering activities other than submarine and alkaline development.

**Samuel Eidensohn** has been appointed to the new post of chief project engineer at Exide Industrial Div., Electric Storage Battery Co., Philadelphia. Dr. Eidensohn, one of the country's outstanding experts on submarine batteries, will supervise company engineering in that field and in the area of alkaline batteries. Formerly he was chief of the battery section of the U. S. Navy's Bureau of Ships.

**Jerome Strauss** is retiring from his position as vice-president of Vanadium Corp. of America after 30 years of service. Active in metallurgical circles for over 40 years, he was in 1953 the ASTM Gillett Memorial Lecturer, and in 1955 the Burgess Memorial Lecturer of the Washington Chapter of ASM. In that same

year he received the Honor Award from his alma mater, Stevens Institute of Technology. Mr. Strauss plans to undertake a limited amount of consulting work both here and abroad, and at present is in Europe in this connection.

**Herman Wissenberg** has joined the staff of Metals Research Labs., Electro Metallurgical Co., Div. of Union Carbide Corp., Niagara Falls, N. Y. Dr. Wissenberg has been assigned to the metals research group where he will work on kinetics of electrode processes.

---

## Letter to the Editor

---

Dear Sir:

In your editorial in the February 1958 JOURNAL you mention the Royal Canadian Navy's experience with cathodic protection. In the discussion you state that more current is needed to maintain the proper potential when the ship is in port than when underway. The opposite is actually true. More current is required when underway due to depolarization effects.

The dual system on some ships came about as a result of the necessity to get increased current to the stern of ships fitted with steel anode impressed current systems on their bilge keels. It is less expensive to fit magnesium anodes with a low value fixed resistor in the attachment to the hull than to extend the steel anodes beyond the bilge keels. On ships with impressed-current inert anode systems where cold bonded neoprene is used on the hull around the anodes as a current shield, the anodes are more widely distributed over the hull and their location ensures proper current distribution to all areas of the hull so that magnesium anodes are not required at the stern.

J. H. Greenblatt  
for Chief Superintendent  
Naval Research Establishment  
Dartmouth, N. S., Canada

---

## News Items

---

### Palladium Medal Award in 1959

The fifth Palladium Medal of The Electrochemical Society will be awarded at the Fall Meeting of the Society in Columbus, Ohio, October 18-22, 1959. The medal was established in 1951 by the Corrosion Division for distinguished contributions to fundamental knowledge of theoretical electrochemistry and of corrosion processes. It is awarded bi-

ennially to a candidate selected by a committee appointed by the Society's Board of Directors. This year the committee members are A. L. Ferguson, H. A. Liebhafsky, T. P. May, E. B. Yeager, and H. A. Laitinen, *Chairman*.

The Committee invites Sections, Divisions, and members of the Society to send suggestions for candidates, accompanied by supporting information, to *H. A. Laitinen, Dept. of Chemistry, University of Illinois, Urbana, Ill.* Candidates may be citizens of any country and need not be members of the Society. Previous medalists have been: Carl Wagner, Massachusetts Institute of Technology [now with Max Planck Institut für Physikalische Chemie]; N. H. Furman, Princeton University, U. R. Evans, Cambridge University; and K. F. Bonhoeffer, Max Planck Institut für Physikalische Chemie (posthumous award).

### Society Fall 1958 Meeting, Ottawa, Canada

For the Fall Meeting of the Society, to be held Sept. 28-Oct. 2, visits are being planned to Atomic Energy (Canada) Ltd. at Chalk River, Ont., and to Dominion Magnesium Ltd., Haley, Ont. These tours will be held on Friday, October 3, 1958, and each will be an all-day trip. The costs will be approximately \$5.00 and \$4.00, respectively, payable at the time of registration at the convention. As only 40 persons can be accommodated on each tour, those who are interested are asked to make their reservations at an early date.

In making a plant tour reservation, full name, address, nationality, and business affiliation should be given. Instructions for convention registration will be given at a later date.

Plant tour reservations should be addressed to Mr. J. S. McCree, Mines Branch, 552 Booth St., Ottawa, Ont., and should be received *before July 30, 1958*.

### 1958 International Conference on Semiconductors

The 1958 International Conference on Semiconductors will be held August 18-22, 1958 at the University of Rochester, Rochester, N. Y.

The aim of the Conference, like that of its predecessors in 1954 (Amsterdam) and 1956 (Garmisch-Partenkirchen), is to discuss some of the fundamental concepts of electronic processes in semiconductors, from the experimental and theoretical standpoint. Special emphasis will be given to basic principles concerning energy

levels, impurity states, and carrier transport.

The Conference is being sponsored by the International Union of Pure and Applied Physics and by the following agencies of the U. S. Government: Air Force Office of Scientific Research, ARDC, Atomic Energy Commission, National Science Foundation, and the Office of Naval Research. Additional support will be provided by various industrial organizations in the United States. The host institution is the University of Rochester.

Among prominent scientists in the semiconductor field from abroad who are planning to attend are the following: P. Aigrain, G. Busch, R. J. Elliott, F. C. Frank, G. F. J. Garlick, A. F. Gibson, E. F. Gross, A. F. Joffe, P. T. Landsberg, G. G. Macfarlane, E. W. J. Mitchell, J. W. Mitchell, S. I. Pekar, D. Polder, A. R. Regel, R. A. Smith, L. Sosnowski, L. S. Stilbans, J. Tauc.

Widespread interest by others from abroad, as well as by scientists in this country, is indicated.

#### Program

The subject matter of the Conference may be inferred from the following typical topics: 1—Band Structure, 2—Lattice Vibrational Spectrum, 3—Recombination and Trapping, 4—Magnetic Resonance, 5—Optical and Magneto-Optical Effects, 6—Galvanomagnetic Effect, 7—Surface States, 8—Impurity Levels, 9—Transport Properties, 10—Structural Defects, 11—Excitons, 12—Thermoelectric Effects.

The emphasis will be on fundamental aspects of these topics rather than applications.

The opening session will be devoted to welcoming remarks by the president of the University of Rochester or his representative and to addresses by J. Bardeen, Chairman of the Conference, as well as other distinguished scientists in the semiconductor field. The final session, which is being organized by C. Herring, will summarize the principal ideas and trends that have come out of the Conference. At other times there will be a maximum of three sessions running simultaneously. Each of the simultaneous sessions will include both longer papers of 25 minutes' duration which will in the main serve to keynote or summarize aspects of the subject under discussion, as well as shorter papers of 15 minutes' duration concerned either with new information or a summary of recent work involving a more specific topic. Some outstanding talks of interest to everyone attending the

Conference may be scheduled so as not to conflict with the simultaneous sessions.

#### Conference Proceedings

The Proceedings are to be published shortly after the end of the year as a single issue of the *Journal of the Physics and Chemistry of Solids*. All regular subscribers to the journal will automatically receive copies. For those attending the Conference the cost of the Proceedings is \$3.00 and is included in the registration fee. Other individuals ordering the Proceedings from Pergamon Press, the publishers, before the end of 1958 will be charged \$4.00. The cost to individuals thereafter will be \$5.00. Single copy rates to libraries and institutions will be higher, but the copies will be bound.

For further information address Conference Secretary, M. H. Hebb, General Electric Co., P. O. Box 1088, Schenectady, N. Y.

#### Dow Develops Process to Recover Gallium

A new process for recovering gallium, one of the less common elements, has been developed and patented by The Dow Chemical Co.

The method consists of treating subdivided ore containing the metallic element with a current of hydrogen chloride or hydrogen bromide under substantially anhydrous conditions at a temperature ranging from 700° to 950°C. The current is utilized in an amount sufficient to volatilize gallium as the trihalide and condensing and recovering it as the pure material.

## Shape of things to Come—in Copper

Plated Moulds, Inc., finds even heavy, intricate molds are plated faster—deposits are smoother, denser, more uniform—with "Plus-4" (Phosphorized Copper) Anodes

"Plus-4"<sup>®</sup> Copper Anodes have helped Plated Moulds, Inc., Yonkers, N. Y., open up new areas of business in electroformed copper molds for the mass production of intricately shaped products in vinyl plastisols.

A leader in the production of copper molds for dolls and toys, Plated Moulds also pioneered in making the molds for plastic footwear. About three years ago, the company tried "Plus-4" Anodes in its tanks with these results:

1. Deposits were uniform, with excellent density. They had experienced some porosity with ordinary anodes.
2. There were far fewer nodules. This was particularly important in building up shells as thick as  $\frac{1}{4}$ ".
3. They could plate faster, using higher current densities.

4. Efficiency in copper use was higher because the anodes corroded more uniformly.

5. Tank maintenance was reduced. There was less sulfate—no sludge.

These advantages made it practical and economical to try larger, heavier molds. The hobbyhorse mold illustrated is one result. And Plated Moulds is moving out into the commercial and industrial fields with molds for motorcycle and bicycle seats, automotive assemblies, display models.

Write for information on how you can obtain a test quantity to supply one tank. Address: The American Brass Company, Waterbury 20, Connecticut. In Canada: Anaconda American Brass Ltd., New Toronto, Ont.

58184

# ANACONDA<sup>®</sup>

## "PLUS-4" ANODES Phosphorized Copper

Made by The American Brass Company

The company says it believes the new process will make possible the extraction of substantial quantities of gallium from ores.

The process is covered by U. S. Patent No. 2,823,096 just issued. The inventors are Dr. L. K. Frevel who holds the title of research scientist and Dr. J. T. Kummer who has the title of research associate. Both are with the company's spectroscopy laboratory.

### Glidden Co. Lectures in Chemistry

Continuation of a lecture program in chemistry at five of the nation's top universities was announced recently by Dr. William von Fischer, coordinator of research and development for The Glidden Co.

Established last year to stimulate a greater interest in chemistry and chemical engineering, the program, known as "The Glidden Company Lectures in Chemistry," was so enthusiastically received that Glidden will continue this activity during the present academic year. Lectures will again be sponsored at the University of Illinois, Ohio State University, University of Michigan, Johns Hopkins University, and the Case Institute of Technology. Also included in the program this year will be the University of Toronto in Canada.

During the past year such outstanding scientists as Professor Linus Pauling of California Institute of Technology; Dr. Bryce L. Crawford, Jr., University of Minnesota; Dean W. R. Marshall, Jr., University of Wisconsin; Professors Ronald S.

Nyholm and C. K. Ingold, University College, London; and Dr. A. Charlesby, Tube Investments Research Labs., have been speakers at the various colleges and universities. Equally outstanding educators will be lecturers during the current year's program.

### Twelfth Annual Battery Research and Development Conference

The Twelfth Annual Battery Research and Development Conference will be held on Wednesday and Thursday, May 21 and 22, 1958, at the Berkeley-Carteret Hotel, Asbury Park, N. J.

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 Engineering Labs., Fort Monmouth, N. J.

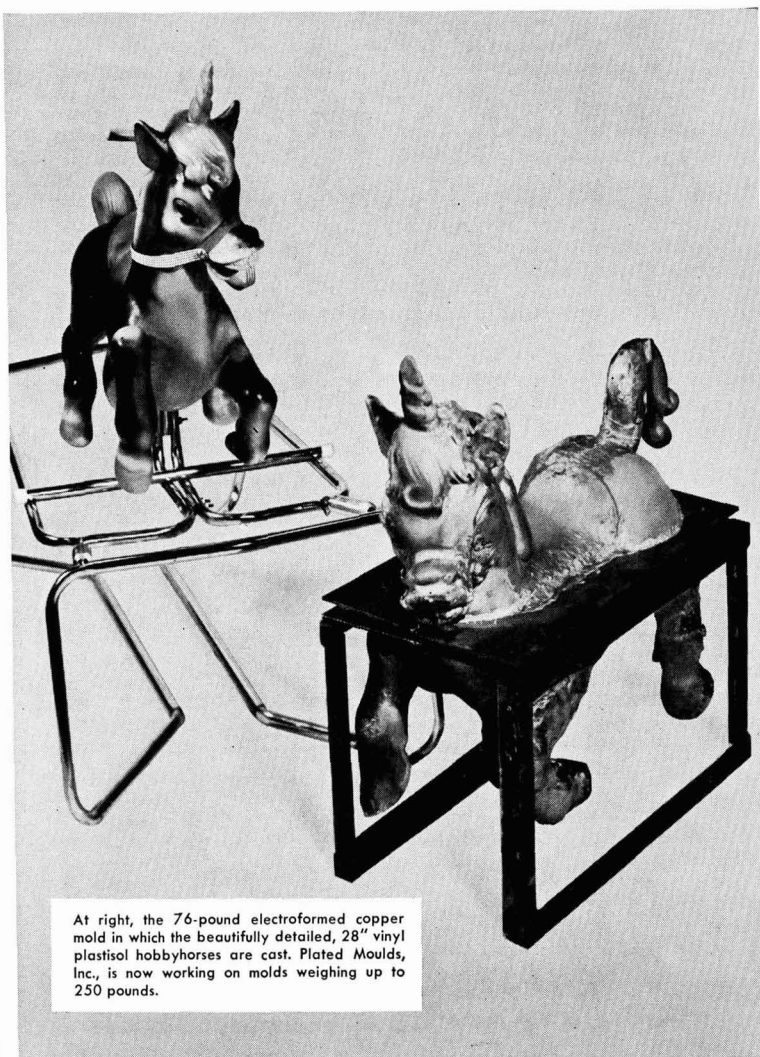
#### Preliminary Program

Arthur F. Daniel, *Chairman*

- Welcoming Remarks—May 21
- Symposium on Fuel Cells—May 21
- Symposium on Primary Batteries:
  - New Primary Battery Designs—May 21; Low Temperature Batteries—May 22
- Symposium on Nickel-Cadmium Batteries—May 21
- Symposium on Special Purpose Batteries: New Battery Systems—May 21; Automatically Activated Zinc-Silver Oxide Batteries—May 22
- Symposium on Power Sources of the Future—May 22
- Cocktail Party—May 21
- Dinner—May 21

### Literature from Industry

**Semiconductor Rectifier Power Conversion Systems**—Bulletin GEA-6684, 16 pages, discusses use of semiconductor rectifier systems for supplying d-c power for electrochemical processes, electroplating, anodizing, aluminum reduction, and copper refining. Publication explains advantages of systems approach, lists features of General Electric systems, describes four methods of meeting d-c power requirements for electrolytic processes, discusses application of power conversion systems, and provides technical data on performance characteristics of General Electric rectifier systems. *General Electric Co., Schenectady 5, N. Y.*



At right, the 76-pound electroformed copper mold in which the beautifully detailed, 28" vinyl plastisol hobbyhorses are cast. Plated Moulds, Inc., is now working on molds weighing up to 250 pounds.

## Announcements from Publishers

"The Effect of Corrosion Preventives on Chromic Acid Films Adsorbed on Phosphate Coatings," W. D. McHenry and J. Doss, Rock Island Arsenal Lab., U. S. Army. Report PB 131296,\* 15 pages, 50 cents.

Chromic acid rinses have been used for many years to enhance the corrosion resistance of phosphate coatings. It was desired to know what effect water displacing and non-water displacing preservatives have on the chromic acid after-treatment of the coatings. In this study it was determined how much chromic acid is removed under various conditions. These data were correlated with corrosion results. Based on test results, it is recommended that after removal from a chromic acid rinse, phosphated steel should be air-blown dry and immersed in a water-displacing preservative. This procedure will provide maximum protection against corrosion.

"Static Electrification of Steel Cartridge Casings with Dielectric Coatings and the MK47 Electric Primer," K. W. Bewig, Naval Research Lab., Oct. 1957. Report PB 131304,\* 7 pages, 50 cents.

Concern had been expressed about the possible hazard from the detonation of electric primers caused by free electrostatic charges residing on cartridge casings. Teflon coatings, used for lubricating and preserving steel casings, in particular had been known to store surface and volume electrostatic charges because of their low conductivity and small loss factor. Tests described in this report proved that chromic oxide-loaded

Teflon coatings on casings are not a hazard to accidental electrostatic detonation of electric primers. They are recommended over epoxy phenolic resin coatings because of their superior lubricating qualities. Clear Teflon coatings, however, will not discharge by grounding because of their low conductivity, and should not be used on cartridge casings.

"Electrical Properties of Irradiated Polymers," R. E. Woodard, Wright Air Development Center, U. S. Air Force, June 1957. Report PB 131254,\* 32 pages, \$1.00.

The effects of nuclear radiation on the electrical properties of polymers were examined as part of R&D efforts to develop improved engineering materials for nuclear powered aircraft and supersonic vehicles. A brief discussion is given of the electronic nature of solids as it applies to insulators and then polymers. The fundamental theory of nuclear radiation is reviewed and shown to be associated with the laws of energy dissipation of radiation particles within a material. The role played by nuclear radiation in polymer kinetics is discussed. Earlier studies of the electrical properties of irradiated polymers are surveyed. An analogy is drawn between photoconductivity in semiconductors and conductivity in certain polymers induced by nuclear radiation. The instantaneous nature of this induced conductivity is emphasized. The change produced in the dielectric constant of an irradiated polymer is considered in terms of crosslinking and dipole moments. Also included is a survey of available engineering data for irradiated polymers.

"A Survey of the Literature on Rhenium," C. T. Sims, E. N. Wyler, G. B. Gaines, and D. M. Rosenbaum, Battelle Memorial Institute, for Wright Air Development Center,

U. S. Air Force, June 1956. Report PB 121826,\* 236 pages, \$4.50.

The aim of this survey was to evaluate and arouse interest in the prospective applications of rhenium. All information accumulating in the literature during the 27 years prior to 1955 is classified into such major fields of interest as the history of rhenium, its occurrence, recovery, and production, and its physical, electronic, chemical, and metallurgical properties. A complete section on the past, present, and future uses of the metal is included. All references, even those of very remote value, are listed in two classifications: references which apply directly to the text and those which have not been used in the text. The authors conclude that the physical metallurgy of rhenium is virtually an unexplored field and offers ample experimental opportunities.

"Alkaline Storage Batteries: An Investigation of Nickel Oxide Positive Plate Characteristics," A. L. Pitman and G. W. Work, Naval Research Lab., Dec. 1957. Report PB 131329,\* 23 pages, 75 cents.

This volume reports part of a continuing project aimed at better understanding, and possible utilization in naval applications, of the alkaline type of storage battery. Positive plate characteristics of the nickel oxides were studied in several different types of cells. It was found that a current efficiency of 95-100% could be attained if oxygen evolution was avoided during charge. Under such conditions, however, the capacity of the positive plate nickel oxide was reduced one-third. A summary of earlier and present work on the electrode showed that the Ni-Ni(OH)<sub>2</sub> and Ni<sub>2</sub>O<sub>3</sub>(OH)<sub>2</sub>-beta NIOOH couples are well defined, while two other possible nickel oxide couples are not. (Two other NRL studies were released earlier through OTS and are

\* Order from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C.

## Manuscripts and Abstracts for Fall 1958 Meeting

Papers are now being solicited for the Fall Meeting of the Society, to be held at the Chateau Laurier in Ottawa, Canada, September 28, 29, 30, October 1, and 2, 1958. Technical sessions probably will be scheduled on Batteries, Corrosion, Electrodeposition (including symposia on "Electrodeposition on Uncommon Metals" and "Chemical and Electropolishing"), Electronics (Semiconductors), Electro-Organics, Electrothermics and Metallurgy, and a symposium on "Films Formed in Contact with Liquids" sponsored by Theoretical Electrochemistry, Battery, and Corrosion Divisions.

To be considered for this meeting, triplicate copies of abstracts (*not to exceed 75 words in length*) must be received at Society Headquarters, 1860 Broadway, New York 23, N. Y., *not later than June 2, 1958. Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

\* \* \*

The Spring 1959 Meeting will be held in Philadelphia, Pa., May 3, 4, 5, 6, and 7, 1959, at the Sheraton Hotel. Sessions will be announced in a later issue.



still available under the general title "Alkaline Storage Batteries: The Self-Discharge of the Positively Charged Nickel Oxide Electrode." The volumes are: PB 121430, "Part 1—The Role of Water in the Process," Oct. 1956, 17 pages, 50 cents; and PB 121483, "Part 2—Potential as a Function of Time on Open Circuit and as a Function of the Active Oxygen on the Nickel Oxide Plates," Oct. 1956, 17 pages, 50 cents.)

"Electrophoretic Deposition of Plutonium, A Feasibility Study," Atomic Energy Commission report, July 1957. Report LA-2153,\* 13 pages, 50 cents.

"Vapor Deposition of Molybdenum and Niobium Coatings on Stainless Steel Tubes," AEC study, Oct. 1957. Report BMI-1228,\* 8 pages, 50 cents.

"The Corrosion of Monel and 70-30 Cupronickel in Hydrofluoric Acid," AEC study, Dec. 1957. Report BMI-1237,\* 21 pages, 75 cents.

"Alloys of Aluminum, Thorium, and Uranium," AEC study, Dec. 1956. Report ISC-832,\* 26 pages, \$1.00.

"The Aqueous Corrosion of Zircaloy Clad Thorium," AEC study, Sept. 1957. Report NMI-1191,\* 25 pages, 75 cents.

"Unclassified U. S. Atomic Energy Commission Reports on the Metallurgy of Zirconium and Hafnium," June 1957. Report TID-3508,\* 37 pages, \$1.00.

"Non-Destructive Testing, A Literature Search," AEC study, Nov. 1957. Report TID-3521,\* 11 pages, 50 cents.

"Corrosion Testing of Zircaloy-2 and Zircaloy-3," AEC study, Oct. 1957. Report WAPD-TM-97,\* 32 pages, \$1.00.

"Hydrogen Redistribution in Thin Plates of Zirconium under Large Thermal Gradients," AEC study, Jan. 1958. Report WAPD-TM-104,\* 33 pages, \$1.00.

### "Metallurgical Applications of the Rare Earths"

Abstracts prepared in a comprehensive survey covering ten years of literature here and abroad on the metallurgical applications, both ferrous and nonferrous, of the rare earths, have been incorporated in a 46-page publication of the Davison Chemical Co., Div. of W. R. Grace & Co.

Principal applications covered are improving the properties of cast iron—particularly for producing a nodular structure; alloying additions to cast and wrought stainless steels; alloying additions to aluminum and magnesium alloys; nonferrous refractory alloys—particularly chromium and nickel alloys; and other metallurgical applications, including the cerium-base pyrophoric alloys and the addition of rare earths to dip-coating baths.

A complimentary copy of the publication, "Metallurgical Applications of the Rare Earths," may be obtained on letterhead application to Davison Chemical Co., P. O. Box 488, Pompton Plains, N. J.

## Employment Situations

Please address replies to box shown, c/o The Electrochemical Society, Inc., 1860 Broadway, New York 23, N. Y.

### 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

## Advertiser's Index

American Brass Company....98C-99C	
Bell Telephone Laboratories, Inc. ....	92C
Delco Radio Division, General Motors Corporation..	94C
Enthone, Incorporated .....	Cover 4
Great Lakes Carbon Corporation .....	Cover 2
Stackpole Carbon Company.....	91C

range from \$4480 per annum to \$8645 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. 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.

**Research Director**—To direct research activities on secondary battery electrode systems. Ph.D. required in physical chemistry, electrochemistry, or experience in those fields. Expanding organization offers challenging opportunity. Reply to Box A-276.

## December 1958 Discussion Section

A Discussion Section, covering papers published in the January-June 1958 JOURNALS, is scheduled for publication in the December 1958 issue. Any discussion which did not reach the Editor in time for inclusion in the June 1958 Discussion Section will be included in the December 1958 issue.

Those who plan to contribute remarks for this Discussion Section should submit their comments or questions in triplicate to the Managing Editor of the JOURNAL, 1860 Broadway, New York 23, N. Y., not later than September 1, 1958. All discussions will be forwarded to the author(s) for reply before being printed in the JOURNAL.



# The Electrochemical Society

## Patron Members

Aluminum Company of Canada, Ltd.,  
Montreal, Que., Canada  
International Nickel Company, Inc.,  
New York, N. Y.  
Olin Mathieson Chemical Corporation,  
Niagara Falls, N. Y.  
Industrial Chemicals Division, Research  
and Development Department  
Union Carbide Corporation  
Divisions:  
Electro Metallurgical Company,  
New York, N. Y.  
National Carbon Company,  
New York, N. Y.  
Westinghouse Electric Corporation,  
Pittsburgh, Pa.

## Sustaining Members

Air Reduction Company, Inc.,  
New York, N. Y.  
Ajax Electro Metallurgical Corporation,  
Philadelphia, Pa.  
Allied Chemical & Dye Corporation  
General Chemical Division,  
Morristown, N. J.  
Solvay Process Division,  
Syracuse, N. Y. (3 memberships)  
Alloy Steel Products Company, Inc.,  
Linden, N. J.  
Aluminum Company of America,  
New Kensington, Pa.  
American Machine & Foundry Company,  
Raleigh, N. C.  
American Metal Company, Ltd.,  
New York, N. Y.  
American Platinum Works, Newark, N. J.  
(2 memberships)  
American Potash & Chemical Corporation,  
Los Angeles, Calif. (2 memberships)  
American Zinc Company of Illinois,  
East St. Louis, Ill.  
American Zinc, Lead & Smelting Company,  
St. Louis, Mo.  
American Zinc Oxide Company,  
Columbus, Ohio  
M. Ames Chemical Works, Inc.,  
Glens Falls, N. Y.  
Auto City Plating Company Foundation,  
Detroit, Mich.  
Bart Manufacturing Company, Bellville, N. J.  
Basic Incorporated, Cleveland, Ohio  
Bell Telephone Laboratories, Inc.,  
New York, N. Y. (2 memberships)  
Bethlehem Steel Company,  
Bethlehem, Pa. (2 memberships)

Boeing Airplane Company, Seattle, Wash.  
Burgess Battery Company, Freeport, Ill.  
(4 memberships)  
C & D Batteries, Inc., Conshohocken, Pa.  
Canadian Industries Ltd., Montreal, Que.,  
Canada  
Carborundum Company, Niagara Falls, N. Y.  
Catalyst Research Corporation, Baltimore,  
Md.  
Chrysler Corporation, Detroit, Mich.  
Columbian Carbon Company, New York,  
N. Y.  
Columbia-Southern Chemical Corporation,  
Pittsburgh, Pa.  
Consolidated Mining & Smelting Company of  
Canada, Ltd., Trail, B. C., Canada  
(2 memberships)  
Continental Can Company, Inc., Chicago, Ill.  
Cooper Metallurgical Associates, Cleveland,  
Ohio  
Corning Glass Works, Corning, N. Y.  
Cramet, Inc., Chattanooga, Tenn.  
Crane Company, Chicago, Ill.  
Diamond Alkali Company, Painesville, Ohio  
(2 memberships)  
Dow Chemical Company, Midland, Mich.  
Wilbur B. Driver Company, Newark, N. J.  
(2 memberships)  
E. I. du Pont de Nemours & Company, Inc.,  
Wilmington, Del.  
Eagle-Picher Company, Chemical Division,  
Joplin, Mo.  
Eastman Kodak Company, Rochester, N. Y.  
Eaton Manufacturing Company, Stamping  
Division, Cleveland, Ohio  
Electric Auto-Lite Company, Toledo, Ohio  
Electric Storage Battery Company,  
Philadelphia, Pa.  
The Eppley Laboratory, Inc., Newport, R. I.  
(2 memberships)  
Federal Telecommunication Laboratories,  
Nutley, N. J.  
Food Machinery & Chemical Corporation  
Becco Chemical Division, Buffalo, N. Y.  
Westvaco Chlor-Alkali Division, South  
Charleston, W. Va.  
Ford Motor Company, Dearborn, Mich.  
General Electric Company, Schenectady,  
N. Y.  
Chemistry & Chemical Engineering  
Component, General Engineering  
Laboratory  
Chemistry Research Department

(Sustaining Members cont'd)

- General Electric Company (cont'd)  
Metallurgy & Ceramics Research  
Department
- General Motors Corporation  
Brown-Lipe-Chapin Division, Syracuse,  
N. Y. (2 memberships)  
Guide Lamp Division, Anderson, Ind.  
Research Laboratories Division, Detroit,  
Mich.
- Gillette Safety Razor Company, Boston, Mass.  
Gould-National Batteries, Inc., Depew, N. Y.  
Graham, Crowley & Associates, Inc., Chicago,  
Ill.
- Great Lakes Carbon Corporation, New York,  
N. Y.
- Hanson-Van Winkle-Munning Company,  
Matawan, N. J. (3 memberships)
- Harshaw Chemical Company, Cleveland,  
Ohio (2 memberships)
- Hercules Powder Company, Wilmington, Del.  
Hooker Electrochemical Company, Niagara  
Falls, N. Y. (3 memberships)
- Houdaille-Hershey Corporation, Detroit,  
Mich.
- Hughes Aircraft Company, Culver City,  
Calif.
- International Business Machines Corporation,  
Poughkeepsie, N. Y.
- International Minerals & Chemical  
Corporation, Chicago, Ill.
- Jones & Laughlin Steel Corporation,  
Pittsburgh, Pa.
- K. W. Battery Company, Skokie, Ill.
- Kaiser Aluminum & Chemical Corporation  
Chemical Research Department,  
Permanente, Calif.  
Division of Metallurgical Research,  
Spokane, Wash.
- Keokuk Electro-Metals Company, Keokuk,  
Iowa
- Libbey-Owens-Ford Glass Company, Toledo,  
Ohio
- P. R. Mallory & Company, Indianapolis, Ind.  
McGean Chemical Company, Cleveland, Ohio  
Merck & Company, Inc., Rahway, N. J.  
Metal & Thermit Corporation, Detroit, Mich.  
Minnesota Mining & Manufacturing  
Company, St. Paul, Minn.
- Monsanto Chemical Company, St. Louis, Mo.  
Motorola, Inc., Chicago, Ill.
- National Cash Register Company, Dayton,  
Ohio
- National Lead Company, New York, N. Y.  
National Research Corporation, Cambridge,  
Mass.
- Norton Company, Worcester, Mass.
- Olin Mathieson Chemical Corporation,  
Niagara Falls, N. Y.  
High Energy Fuels Organization  
(2 memberships)
- Pennsalt Chemicals Corporation,  
Philadelphia, Pa.
- Philips Laboratories, Inc., Irvington-on-  
Hudson, N. Y.
- Pittsburgh Metallurgical Company, Inc.,  
Niagara Falls, N. Y.
- Poor & Company, Promat Division,  
Waukegan, Ill.
- Potash Company of America,  
Carlsbad, N. Mex.
- Radio Corporation of America, Harrison, N. J.
- Ray-O-Vac Company, Madison, Wis.
- Raytheon Manufacturing Company,  
Waltham, Mass.
- Reynolds Metals Company, Richmond, Va.  
(2 memberships)
- Shawinigan Chemicals Ltd., Montreal, Que.,  
Canada
- Speer Carbon Company  
International Graphite & Electrode  
Division, St. Marys, Pa. (2 memberships)
- Sprague Electric Company, North Adams,  
Mass.
- Stackpole Carbon Company, St. Marys, Pa.  
(2 memberships)
- Stauffer Chemical Company, Henderson,  
Nev., and New York, N. Y. (2 memberships)
- Sumner Chemical Company, Division of  
Miles Laboratories, Inc., Elkhart, Ind.
- Superior Tube Company, Norristown, Pa.
- Sylvania Electric Products Inc., Bayside,  
N. Y. (2 memberships)
- Sarkes Tarzian, Inc., Bloomington, Ind.
- Tennessee Products & Chemical Corporation,  
Nashville, Tenn.
- Texas Instruments, Inc., Dallas, Texas
- Titanium Metals Corporation of America,  
Henderson, Nev.
- Udylite Corporation, Detroit, Mich.  
(4 memberships)
- Upjohn Company, Kalamazoo, Mich.
- Victor Chemical Works, Chicago, Ill.
- Wagner Brothers, Inc., Detroit, Mich.
- Weirton Steel Company, Weirton, W. Va.
- Western Electric Company, Inc., Chicago, Ill.
- Wyandotte Chemicals Corporation,  
Wyandotte, Mich.
- Yardney Electric Corporation, New York,  
N. Y.

***How to make rust-and-scale removal an exact science:*** For more than 20 years, Enthone has studied metal finishing problems and developed specialized solutions. Among the rust and scale removal compounds perfected by Enthone research and proved in the field, are the Alka-Deox<sup>®</sup> series of alkaline materials which electrolytically or non-electrolytically remove rust and scale from steel, cast or malleable iron; Enthol<sup>®</sup> 42, a solvent acid cleaner for steel, zinc, aluminum and other metals; and Actane<sup>®</sup> 70, a replacement for hydrofluoric acid as a dispersing agent in acid pickles to remove colloidal and siliceous films from metals. Write us about your special oxide removal problems. Chances are we have the answer in stock. Enthone, Inc., 442 Elm Street, New Haven 11, Connecticut.



ENTHONE, INC. IS A SUBSIDIARY OF AMERICAN SMELTING AND REFINING COMPANY

**ENTHONE**