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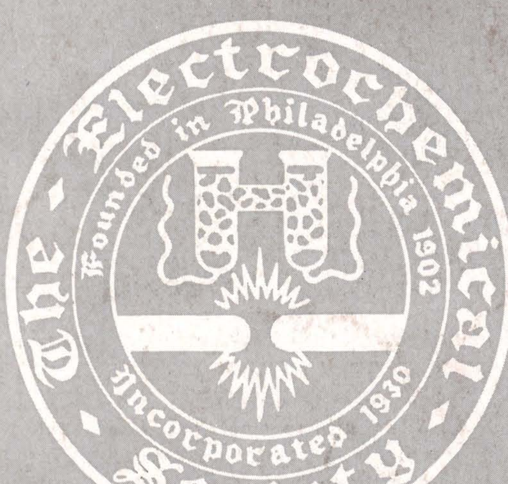

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JULY 1954 **VOL. 101 • NO. 7**

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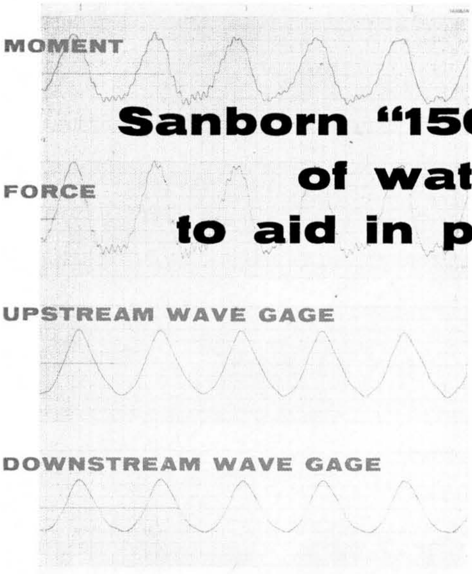
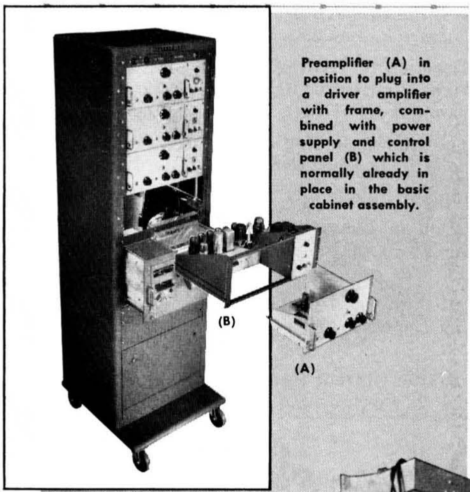
Sanborn "150" records the effects of water wave forces to aid in pile structure design



By means of a Sanborn 150 Oscillographic Recording System equipped with four carrier type preamplifiers, engineers at the M.I.T. Hydrodynamics Laboratory are getting accurate pictures of simulated shallow water waves and their effect on dummy piles. The shape and length of precisely controlled waves in a 90 foot glass flume are plotted simultaneously with their moment and force on a suspended cylindrical pile. The excellent frequency response available with this method permits a sensitivity and accuracy not obtainable in previous model studies of this type.



Preamplifier (A) in position to plug into a driver amplifier with frame, combined with power supply and control panel (B) which is normally already in place in the basic cabinet assembly.

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Virtually all electrical phenomena, within a frequency range of zero to 100 cps, can be accurately, permanently and graphically registered by Sanborn Oscillographic Recording Systems. This versatility of application is possible because of the *flexibility* of Sanborn 150 Series Recording Systems. A wide variety of quickly *interchangeable* preamplifiers, which plug in to *built-in* driver amplifiers (illustrated at left), are available for use with Series 150 Systems, to record such phenomena as: stress, strain, pressure, displacement, thickness, velocity, acceleration, current, voltage, temperature, torque, light, flow, force, load, position, rpm, radiation, tension, and power.

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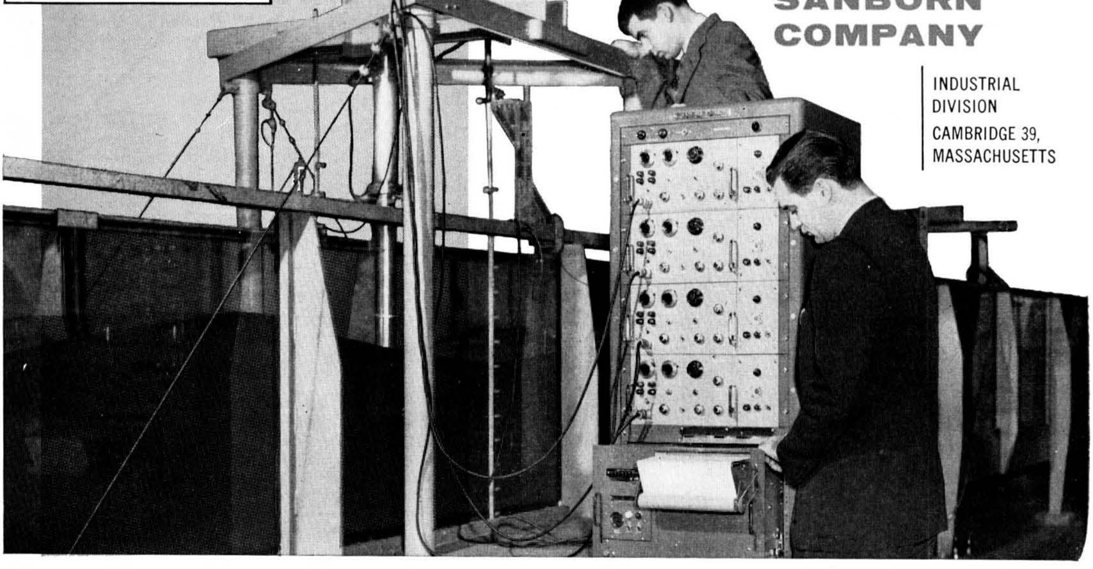

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Sodium Bifluoride

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Ammonium Fluoborate
Potassium Fluoborate
Sodium Fluoborate

ALKALI FLUORIDES
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Calcium Fluoride
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Cupric Fluoride
Ferric Fluoride
Lead Tetrafluoride
Magnesium Fluoride (Not Optical Grade)
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Manganese Trifluoride
Molybdenum Hexafluoride
Nickelous Fluoride
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Trifluoromethane (Fluoroform)	CHF_3
Monochlorotrifluoromethane	$CClF_3$
Fluoroethanes	
Difluoroethane (Ethylidene fluoride)	$CH_3 \cdot CHF_2$
Difluoromonochloroethane	$CH_3 \cdot CClF_2$
Tetrachlorodifluoroethane	$CCl_3 \cdot CClF_2$
Monochlorotrifluoroethane	$CH_2Cl \cdot CF_3$
Trichlorotrifluoroethanes	$CCl_2F \cdot CClF_2$ $CCl_3 \cdot CF_3$
Dichlorotetrafluoroethanes	$CClF_2 \cdot CClF_2$ $CCl_2F \cdot CF_3$
Monochloropentafluoroethane	$CClF_2 \cdot CF_3$
Fluoroethylenes	
Difluoroethylene (Vinylidene fluoride)	$CH_2 = CF_2$
Dichlorodifluoroethylene	$CCl_2 = CF_2$
Trifluorochloroethylene	$CClF = CF_2$
Monochlorodifluoroethylene	$CHCl = CF_2$
Fluorobromoethanes	
Dibromodifluoroethane	$CH_2Br \cdot CBrF_2$
Fluorinated Acetic Acids and Anhydrides	
Dichloromonofluoroacetic acid and anhydride	CCl_2FCOOH and $(CCl_2FCO)_2O$
Monochlorodifluoroacetic acid and anhydride	$CClF_2COOH$ and $(CClF_2CO)_2O$
Fluorinated Acetones	
Tetrachlorodifluoroacetone	$CCl_2F \cdot CO \cdot CCl_2F$
Trichlorotrifluoroacetone	$CCl_2F \cdot CO \cdot CClF_2$
Dichlorotetrafluoroacetone	$CClF_2 \cdot CO \cdot CClF_2$

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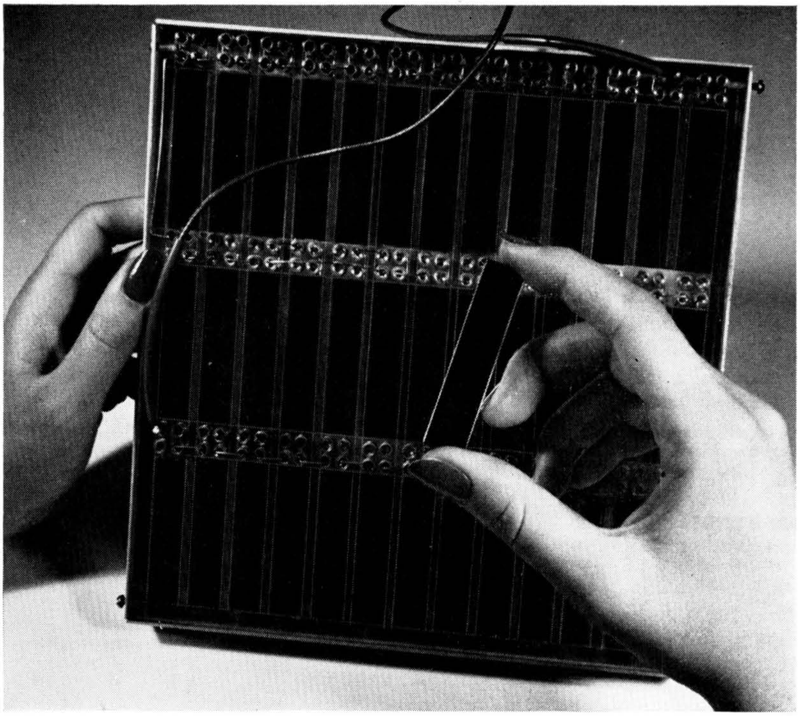
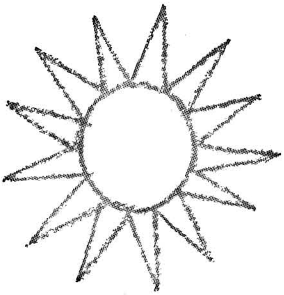


The Bell Solar Battery. A square yard of the small silicon wafers turns sunshine into 50 watts of electricity. The battery's 6% efficiency approaches that of gasoline and steam engines and will be increased. Theoretically the battery will never wear out. It is still in the early experimental stage.



Bell Solar Battery

Bell Laboratories scientists have created the Bell Solar Battery. It marks a big step forward in converting the sun's energy directly and efficiently into usable amounts of electricity. It is made of highly purified silicon, which comes from sand, one of the commonest materials on earth.

The battery grew out of the same long-range research at Bell Laboratories that created the transistor—a pea-sized amplifier originally made of the semiconductor germanium. Research into semiconductors pointed to silicon as a solar energy converter. Transistor-inspired techniques developed a silicon wafer with unique properties.

The silicon wafers can turn sunlight into electricity to operate low-power mobile telephones, and charge storage batteries in remote places for rural telephone service. These are but two of the many applications foreseen for telephony.

Thus, again fundamental research at Bell Telephone Laboratories paves the way for still better low-cost telephone service.

Inventors of the Bell Solar Battery, left to right, G. L. Pearson, D. M. Chapin and C. S. Fuller — checking silicon wafers on which a layer of boron less than 1/10,000 of an inch thick has been deposited. The boron forms a "p-n junction" in the silicon. Action of light on junction excites current flow.

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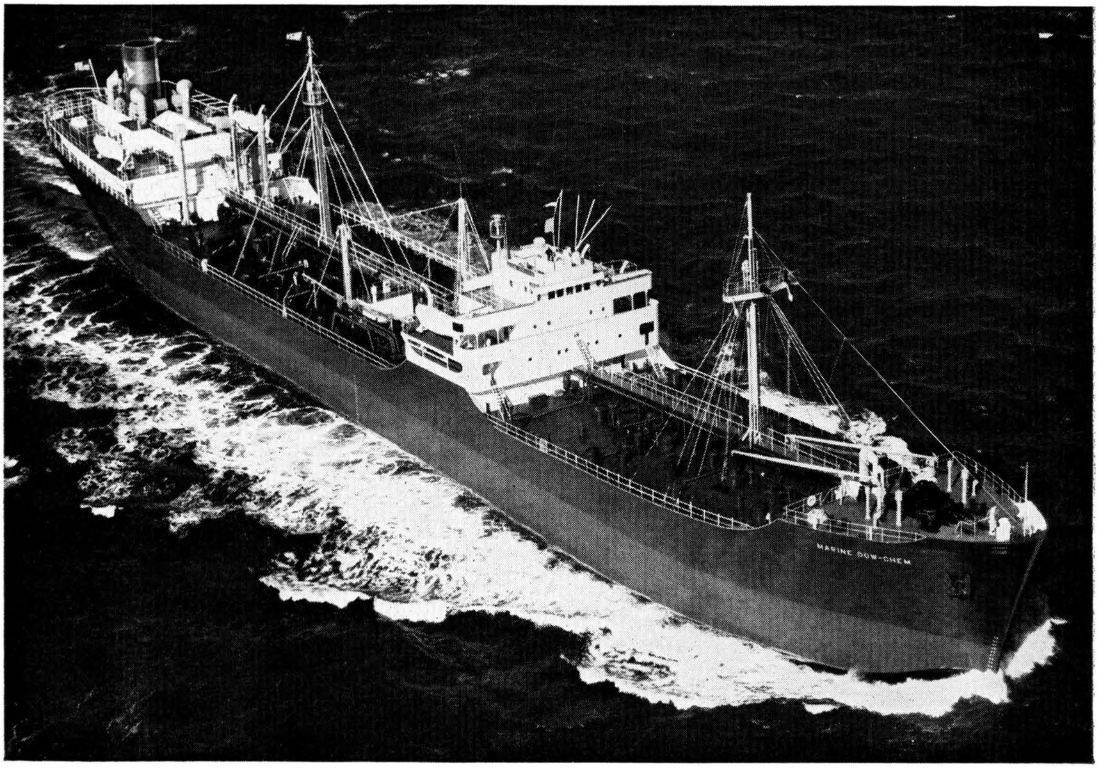

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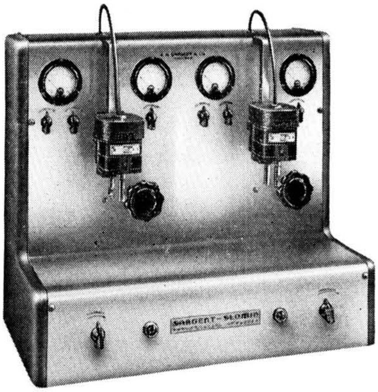

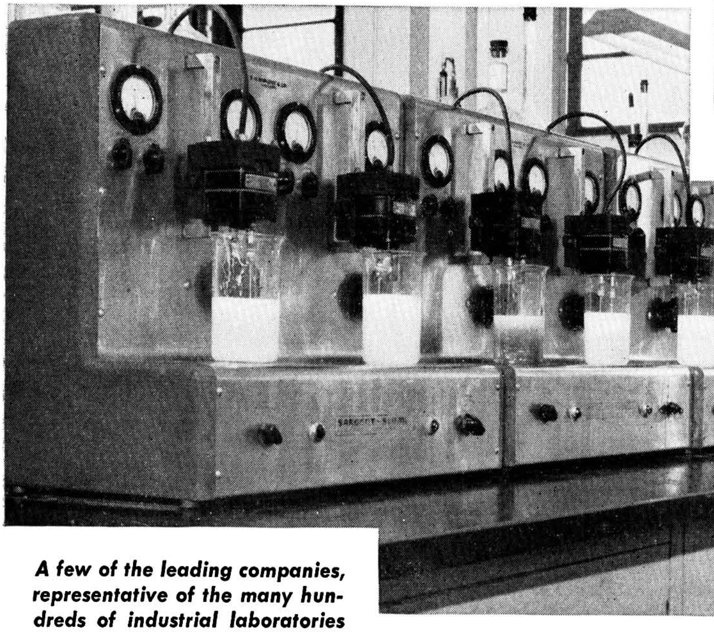

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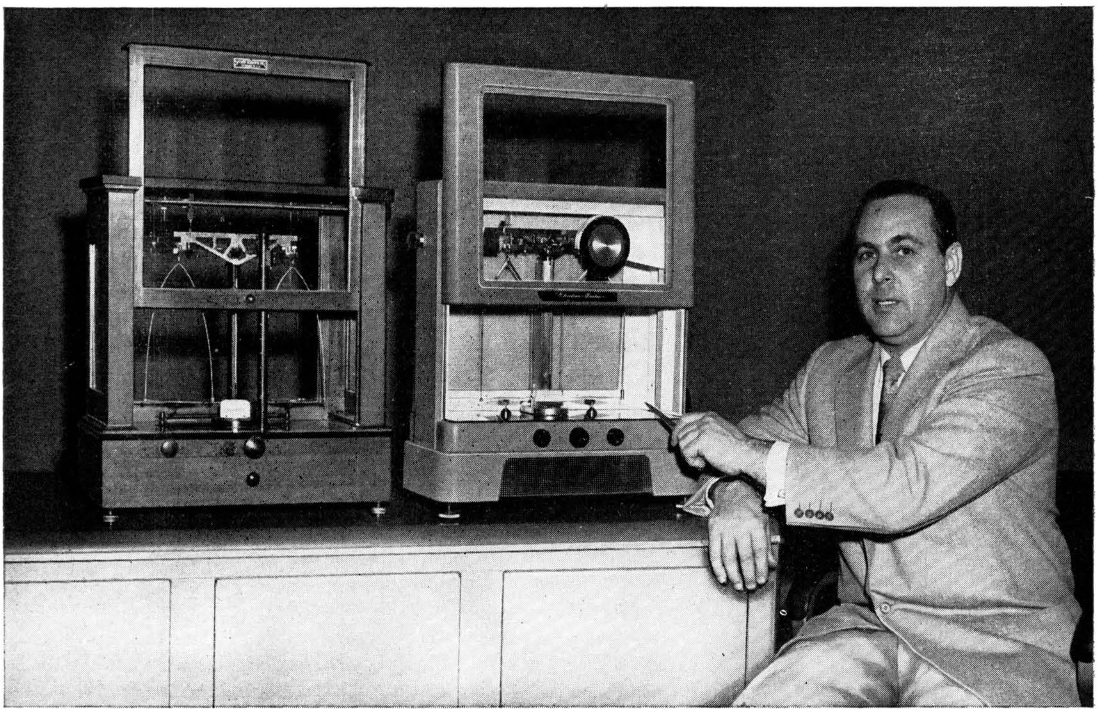

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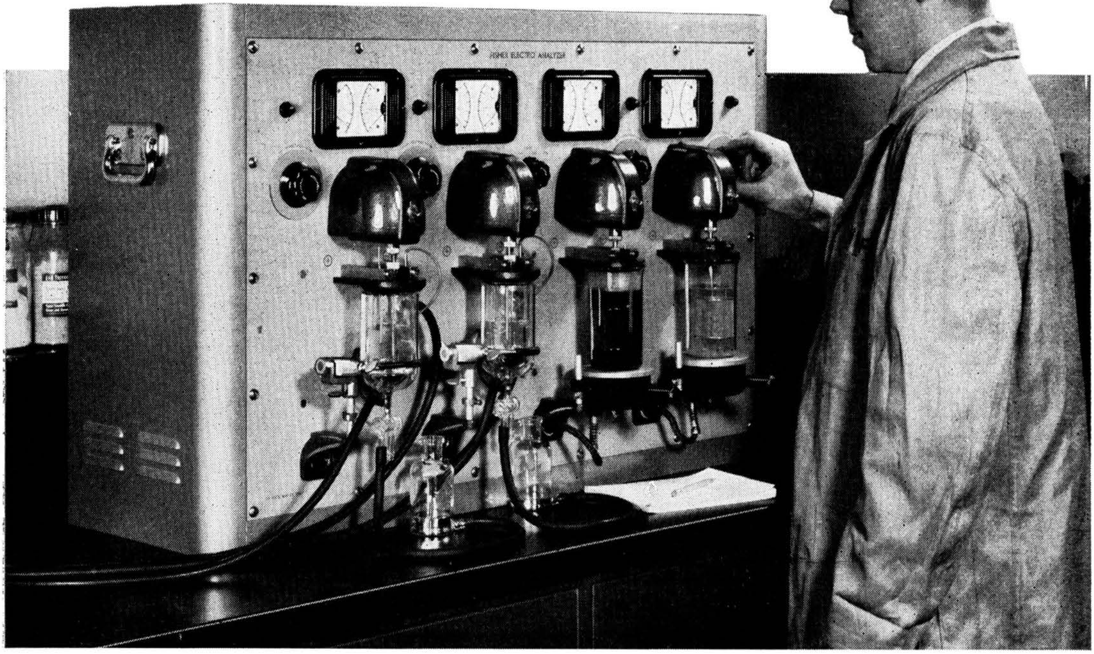

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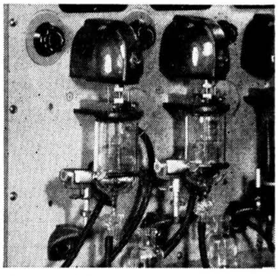
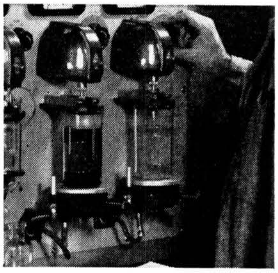


At two left hand spindles, mercury cathode cells remove interfering elements.



At two right hand spindles, heaters bring other samples to optimum temperatures.

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FISHER SCIENTIFIC

Editorial

“But We Were Born Free”

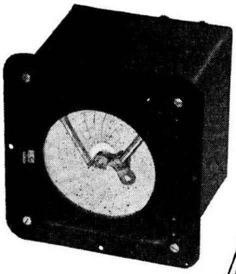
THE catastrophic destructiveness of thermonuclear weapons imposes a new order of urgency for the exercise of intelligence and common sense at both community and national levels. More than ever before, this is a time for clear thinking and rational behavior. This is a time when men trained in science, engineering, and the humanities should contribute in sensible directions to public opinion. Intelligent people are not indifferent toward book burning, witch hunting, and the machinations of self-appointed censors and bigots who would destroy the public school system as they seriously threatened in Pasadena, California, and Englewood, New Jersey. Thoughtful citizens are not deceived by the antics of a calculating political demagogue bent upon enhancing his personal power by exciting public fears.

There is nothing new in the suggestion that scientists and engineers should participate in civic and political affairs to the community’s benefit. They themselves may derive considerable practical education from the experience. The political naiveté of many scientists is well known and often demonstrated. These men of free, independent, and creative minds are an important national asset, but political immaturity invites predatory headline hunters who never hesitate to ruin reputations, if by so doing their own ambitions are advanced.

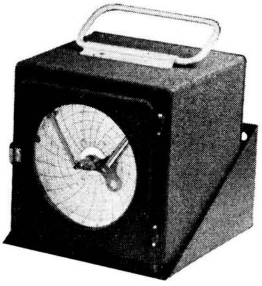
In painful contrast to these more brilliant individuals are the regretable examples of college-trained people in every community who have had no recent experience in the use of their minds. These citizens are likely to join their gullible neighbors in accepting without question current political hokum or the testimonials of satisfied customers respecting the virtues of patent medicines, battery additives, or magical corrosion inhibitors. Unable to discern the threat of a junior Hitler on the political horizon their characteristic response to an anxious questioner is: “While I don’t exactly approve of his methods, I am in favor of what he is trying to do.”

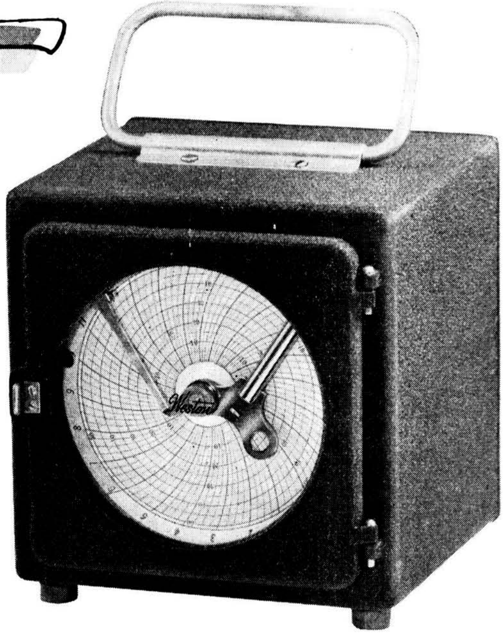
It is remarkable that, in spite of the diverse elements of the population, the thoughtful and the stupid, the reasonable and the fanatic, the sensible and the “superpatriot,” the loyal and the subversive, the country achieves sufficient unity of purpose to manage its affairs. Manifestly, this is democracy in action and the consequence of the freedom of all individuals to believe and express themselves as they choose on all matters without fear of disgrace or liquidation. “But We Were Born Free,” the provocative title of Elmer Davis’ new book, is a timely reminder. Our freedom must be preserved at all costs in these critical times, for free men will always prevail.

—RMB



New





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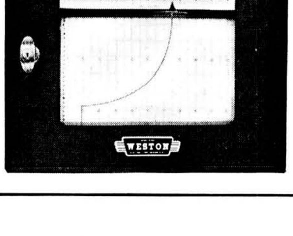

WESTON
Instruments

Kinetics of the High Temperature Oxidation of Zirconium[1]

JACK BELLE AND M. W. MALLETT

Battelle Memorial Institute, Columbus, Ohio

ABSTRACT

The rate of oxidation of high purity zirconium was determined for the temperature range of 575° to 950°C at 1 atm pressure. Data can be fitted to a cubic law and the rate constant in $(\text{ml/cm}^2)^3/\text{sec}$ has been calculated to be $k = 3.9 \times 10^6\ e^{-47{,}200/RT}$, where 47,200 ± 1,000 cal/mole is the activation energy for the reaction.

INTRODUCTION

The early work on the oxidation of zirconium has been reviewed by Gulbransen and Andrew (1) who studied the reaction. Cubicciotti (2) also investigated the oxidation of zirconium recently. Each study involved the use of thin zirconium foil, approximately 0.005 in. thick, for specimens. Hafnium content of the zirconium was approximately 3% in both cases. Gulbransen and Andrew worked in the temperature range of 200°–425°C at an oxygen pressure of 7.6 cm, while Cubicciotti investigated the reaction at 600°–920°C at pressures ranging from 0.1 mm to 20.2 cm. Gulbransen and Andrew stated that the oxidation reaction could not be fitted to any simple rate law over a wide temperature range, but assumed the reaction to follow the parabolic law with initial deviations. Cubicciotti reported that oxidation curves were parabolic at all temperatures except 920°C, where a small deviation toward a linear rate was observed. Energies of activation found by these investigations were 18,000 cal/mole by Gulbransen and Andrew and 32,000 cal/mole by Cubicciotti.

To supplement previous work done largely at lower temperatures and pressures, this study was made in the temperature range 575°–950°C at an oxygen pressure of 1 atm, using low-hafnium zirconium (0.01 weight %).

EXPERIMENTAL

Method.—Rate of reaction between zirconium and oxygen was determined by measurement of the rate of consumption of the gas by the metal at high temperature. The apparatus used was similar to that described in an earlier paper (3) with a few modifications. A 4-kw tungsten-gap-type Lepel converter was used to heat the metal. The zirconium specimen was supported at the bottom by a Vycor stand in the reaction tube, and a platinum-platinum + 10% rhodium thermocouple was welded to the top of the sample. The thermocouple was calibrated against an optical pyrometer in the same manner as for some previous work reported from this laboratory (3).

Zirconium specimens were machined cylinders of two sizes, about 4 cm long by 0.7 cm in diameter and about 5 cm long by 1.4 cm in diameter. Specimens were abraded with kerosene-soaked 240-, 400-, and 600-grit silicon carbide papers and washed in successive baths of naphtha, ether, and acetone.

After placement in the reaction tube, a specimen was degassed by heating to 800°C or higher for 1 hr in a vacuum in order to remove hydrogen prior to the addition of oxygen. Oxygen was added to the reaction tube to atmospheric pressure in measured amounts from a 50-ml glass buret. Pressure measurements were made every 2 min at the start of each run and at longer time intervals as the reaction rate decreased. Oxygen, present in the apparatus as a gas phase, was determined from pressure measurements on a full-length open-end mercury manometer and the calibrated dead space of the system. After the reaction had been followed for the desired time, the system was evacuated and the specimen was cooled to room temperature in vacuum.

The difference between the quantity of oxygen added and that remaining in the gas phase was the quantity reacted with the specimen. The original geometrical dimensions of the specimen were used to compute the quantity of gas reacted per unit surface area.

Materials.—The pure zirconium used in these experiments was de Boer-process iodide crystal bar which had been double arc melted, forged to 1⅛ in.[2] at 1450°F, hot rolled at 1450°F, and cold rolled into ⅜-in. and ⅝-in. diameter rods. Test specimens were machined from these rods. Impurities in the zirconium were determined by spectrographic, chemical, and vacuum-fusion analyses. Weight percentages of the principal impurities detected were: silicon, 0.03; iron, 0.020; hafnium, 0.010; oxygen, 0.01; nitrogen, 0.001; and hydrogen, 0.003.

Oxygen used in this study was prepared from degassed potassium permanganate by the method

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[1] Manuscript received October 22, 1953. Work performed under AEC Contract W-7405-eng-92.

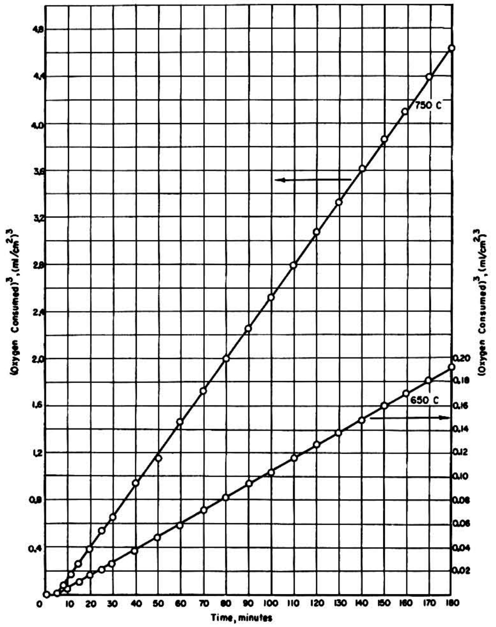

FIG. 1. Reaction of zirconium with oxygen (ml O_2, STP, consumed/cm² metal surface)³ vs. time.

described by Hoge (4). The gas was dried by passing through a dry ice-acetone cold trap.

RESULTS

Measurements of rates of consumption of oxygen by zirconium were made from 575°–950°C at 1 atm pressure. Data below 575°C could not be obtained with the apparatus because of the slowness of the reaction. Above 950°C, the rapidity of the reaction made it difficult to control and often resulted in cracking of the oxide film. Fig. 1 shows typical results of measurements for two temperatures. It was found that the data could not be fitted to the parabolic law, but, except for slight initial deviations, could be represented by a cubic law, $w^3 = kt$, where w = ml (STP) of oxygen consumed per unit surface area. Thus, Fig. 1 is a plot of the cube of the quantity of oxygen consumed per unit surface area against time, and it is seen that the data fall on straight lines. Also, for a cubic oxidation, a graph of log w vs. log t should be a straight line with slope equal to 0.33. Fig. 2 shows such plots for several other

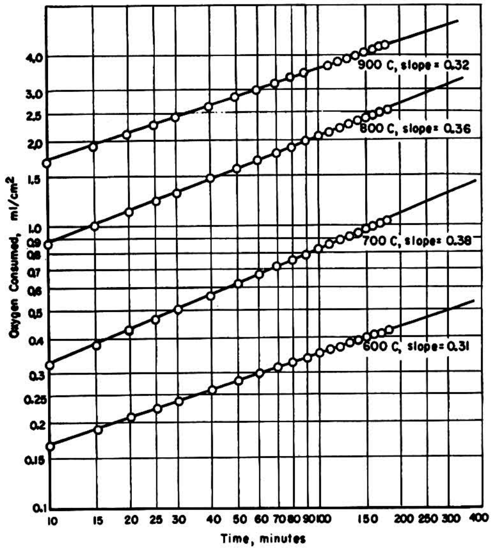

FIG. 2. Log of oxygen consumed in ml/cm² vs. log of time in minutes for 600°, 700°, 800°, and 900°C.

TABLE I. *Rate constants for the reaction of zirconium with oxygen*

Temp, °C ± 5°	Rate constant (k) (ml/cm²)³/sec	Slope of log-log plot
575	2.1×10^{-6}	0.32
600	7.1×10^{-6}	0.31
625	1.4×10^{-5}	0.39
650	1.8×10^{-5}	0.38
675	5.8×10^{-5}	0.39
700	1.0×10^{-4}	0.38
725	1.9×10^{-4}	0.38
750	4.4×10^{-4}	0.36
775	5.5×10^{-4}	0.33
800	1.6×10^{-3}	0.36
825	7.9×10^{-4}	0.33
850	1.6×10^{-3}	0.34
875	3.0×10^{-3}	0.32
900	7.7×10^{-3}	0.32
920	7.6×10^{-3}	0.35
950	2.1×10^{-2}	0.32

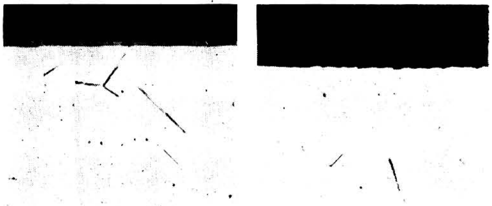

FIG. 3. Structure at surface of zirconium reacted with oxygen. (Note single surface-oxide layers. Needle-like inclusions probably are hydride.) Left, zirconium reacted with oxygen at 575°C for 3 hr. Surface layer about 0.0002 cm thick. Note absence of region of solid solution of oxygen in zirconium. Polished with Linde "B" suspended in chromic acid, then chemically polished in acid solution ($45HNO_3$, $45H_2O$, and 10HF); right, zirconium reacted with oxygen at 825°C for 3 hr. Surface oxide layer about 0.0015 cm thick. Polished with Linde "B" suspended in chromic acid and then etched (etchant: 49 lactic acid, 49 nitric acid, and 2HF). The narrow gray band is ZrO_2, below it is solid solution of oxygen in zirconium. Both 500 ×.

temperatures, and it is seen that good agreement is obtained with the cubic-law expression. Values of the rate constant, k, calculated from various plots and slopes of the log-log plots, are given in Table I.

At the end of a reaction run, the specimen was cooled in vacuum and examined. In all cases throughout the temperature range investigated, reacted specimens were covered with a shiny gray-black coating which adhered very strongly to the metal. Metallographic examination showed that a single oxide layer was present on the surface. This can be seen from the two photomicrographs in Fig. 3. X-ray patterns taken at room temperature indicated that the film was the monoclinic form of ZrO_2. In agreement with the observation of Cubicciotti (2), it was noticed that white spots appeared on the black coating. The white spots, however, did not show up, even at the higher temperatures, within the 3-hr reaction period generally used in the present investigation. However, they did form after long-time runs at all temperatures. Above 1000°C, where the results were erratic, a flaky white coating sometimes formed on top of the gray-black oxide film.

The microstructure of the high temperature specimens, such as that for 825°C shown in Fig. 3, gave evidence of a region of solid solution of oxygen underlying the surface oxide. Ordinarily, this could

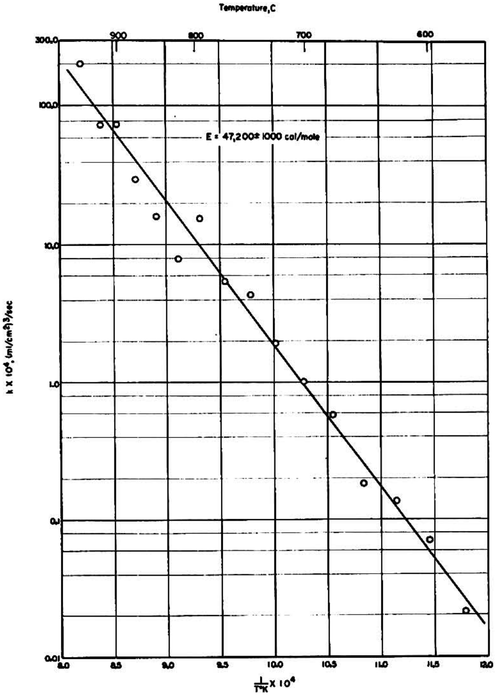

FIG. 4. Zirconium-oxygen reaction—variation of reaction rate constant with temperature.

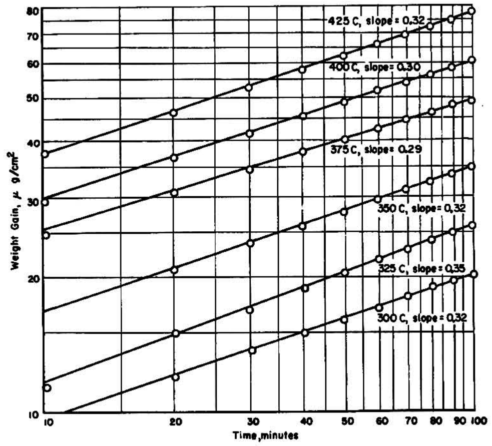

FIG. 5. Log of weight gain in $\mu g/cm^2$ vs. log of time in minutes. Data read from plot (Fig. 3) in paper by Gulbransen and Andrew (1).

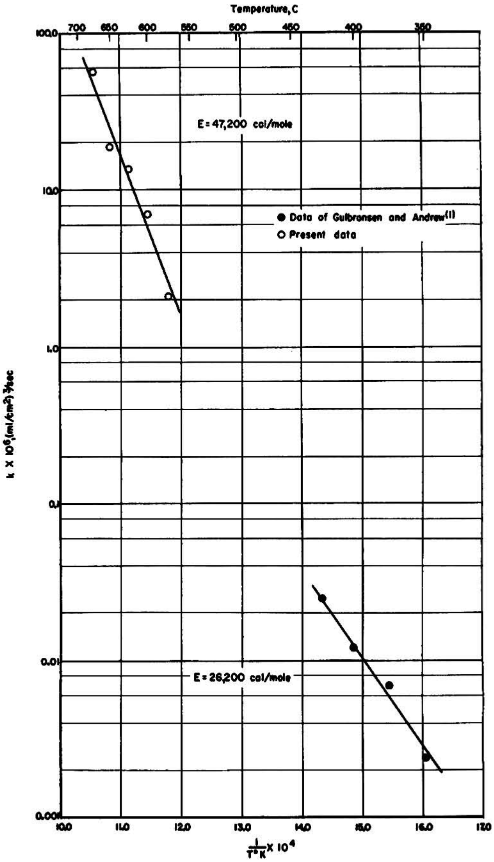

FIG. 6. Zirconium-oxygen reaction—comparison of present data with those of Gulbransen and Andrew.

not be observed metallographically. However, zirconium almost inevitably contains a trace of hydrogen which is manifested as a precipitate within the grains or at grain boundaries. The solution of considerable oxygen appears to displace hydrogen with the result that the solid-solution region is seen as a structureless zone under the microscope.

The effect of temperature on the rate of oxidation can be seen from Table I and Fig. 4. In Fig. 4, the logarithm of the cubic rate constant is plotted as a function of the reciprocal of the absolute temperature. The equation of the best straight line through the points from 575°–950°C was determined by the method of least squares. The experimental energy of activation and the frequency factor were calculated from the Arrhenius-type equation, $k = Ae^{-Q/RT}$. The energy of activation was calculated to be 47,200 ± 1,000 cal/mole. The rate constant in $(ml/cm^2)^3/sec$ is $k = 3.9 \times 10^6 e^{-47,200/RT}$.

DISCUSSION

Gulbransen and Andrew (1) reported that the zirconium oxidation reaction was not initially parabolic, but tended toward parabolic as the reaction proceeded. Limiting slopes at long times were used to calculate rate constants. Although arbitrary, this procedure does have merit if the initial deviations are slight and oxidation times long. However, if the oxidation data of Gulbransen and Andrew (1) (Fig. 3 of their paper) are plotted on a log-log basis, conformity with a cubic law is suggested. This is shown in Fig. 5 where the logarithm of weight gain in $\mu g/cm^2$ is plotted against the logarithm of time. Slopes very close to the theoretical 0.33 are obtained. Rate constants were calculated from straight-line plots of the cube of the weight gain vs. time. These rate constants are compared with the present data in Fig. 6.[2] Straight lines drawn through the separate points are of markedly different slope. The activation energy for the reaction from the data of Gulbransen and Andrew was calculated from the slope of the line in Fig. 6. The value obtained is 26,200 cal/mole as compared with the value of 47,200 cal/mole calculated from the present data. The data of Cubicciotti (2) could not be interpreted in terms of the cubic law. Therefore, no comparison can be made with the present data.

According to the Mott and Cabrera (5) theory of the oxidation of metals, rate of formation of thin oxide films can be expressed by a cubic law for those metals whose oxides are *P*-type semiconductors. (ZrO_2 is probably an *N*-type semiconductor.) The same mechanism, of course, cannot be used to explain the present rate data for formation of thick films during the high temperature oxidation of zirconium. Recent work by Charlesby (6) on the formation of thin oxide films formed electrolytically on metals indicated that a cubic law of oxidation can prevail over a short range of temperatures. No correlation can be made, however, with the present data for the high temperature oxidation of zirconium and the data of Charlesby (7) for the thin anodized oxide films on zirconium.

Waber (8), citing some oxidation data of titanium and tantalum, suggested that the cubic law of oxidation may have a greater range of applicability than has hitherto been expected. The present work appears to be the first experimental evidence to date that this growth law can prevail over a wide temperature range.

ACKNOWLEDGMENT

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1955 issue of the JOURNAL.

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[2] Units of the calculated rate constants from the data of Gulbransen and Andrew were converted to $(ml/cm^2)^3/sec$ for comparison with the present data.

Electrodeposition of Bismuth[1]

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ABSTRACT

Bismuth metal of high purity has been electrodeposited from molten mixtures of bismuth trioxide (10% and 25%) and the eutectic mixture of sodium and calcium chlorides. The rate of metal recovery (g/hr) is good. Energy consumption, based solely on the electrolysis and not on the furnace requirements, is approximately 1 kwhr/lb of bismuth.

INTRODUCTION

Bismuth metal occurs chiefly in nature as bismite, largely Bi_2O_3, and as bismuthinite or bismuth glance, largely Bi_2S_3. The National Production Authority regards bismuth as a "critical" metal chiefly because (*a*) it is important to the defense program of the federal government, and (*b*) high grade ores of the metal are not abundant. However, the total yearly production, according to Leighou (1), is only 2000 tons. In spite of such low tonnage, the metal finds extensive use in the preparation of matrix metal for holding dies and in the preparation of fusible alloys which are employed in making safety plugs in boilers, automatic sprinkling devices, electric fuses, etc. The fact that the metal is able to confer upon alloys its property of expanding on solidification has been responsible for the use of some of its fusible alloys as casting material for statuettes and in dental work.

Several investigators (2) have studied the electrodeposition of bismuth from aqueous solutions on a small scale. Some baths from which the metal has been obtained in reasonably good yields employed nitric acid, hydrochloric acid, or perchloric acid as solvent. Very few studies have been concerned with the electrodeposition of bismuth from molten materials. Drosbach (3) used graphite electrodes and electrolyzed molten $BiCl_3$ in a U-tube type cell of clear glass for 16 hr at a temperature at 340°C and at a current strength of 2 amp. The cathode, 8 mm in diameter, was immersed in the melt to a depth of about 40 mm. Cathode current efficiency was 49.3%. The phase diagram for the system, $BiCl_3$-Bi, is such that the metal is obtained only after prolonged electrolysis. As the metal electrodeposits at the cathode, it dissolves in the molten $BiCl_3$. Eventually, the monochloride (BiCl) forms and, at 320°C, there result two layers. After prolonged electrolysis and subsequent cooling of the melt, bismuth metal is isolated by remelting the metal-rich layer under NaCl.

Industrially, the metal is obtained chiefly by reduction of oxide ores with carbon or iron in crucibles (4) or in small reverberatory furnaces, in the presence of a suitable flux, and by an aqueous electrolysis process (5) that makes use of the anode slimes at electrolytic lead and tin refineries.

The present research was undertaken in order to study the electrodeposition of bismuth from mixtures of Bi_2O_3 and the NaCl-$CaCl_2$ eutectic and to estimate whether electrometallurgy of this sort would be superior to and/or more economical than existing methods for producing the metal. A choice of the eutectic mixture as solvent was based on the following, viz., (*a*) the molten material is an excellent conductor (6) of the electric current; (*b*) the component salts are extremely cheap; (*c*) the metal of each salt is considerably more active than bismuth; and (*d*) the melting point (505°C) of the eutectic mixture (51.8 mole % NaCl; 48.5 mole % $CaCl_2$) is relatively low by comparison with the melting points of the components (NaCl, mp is 798°C; $CaCl_2$, mp is 770°C).

EXPERIMENTAL

Preliminary Studies

Some phase studies were made first since it was important to determine the solubility of Bi_2O_3 in the NaCl-$CaCl_2$ eutectic mixture. Also, it was necessary to know the influence of the oxide upon the electrical conductivity of the eutectic mixture.

Solubility studies.—Mixtures, of Bi_2O_3 and the NaCl-$CaCl_2$ eutectic or of Bi_2O_3 and NaCl, of known composition were placed in 250 ml porcelain crucibles and heated to 950°C in a pyrometer-controlled electric crucible furnace (chamber diameter, 8 in.;

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chamber depth, 18 in.). Mixtures containing from 25–30% Bi_2O_3 formed pastes which did not liquefy at temperatures 200° higher than the melting point of the solvent. In the early stages of the work, melts containing up to about 25% Bi_2O_3 in either NaCl or eutectic appeared homogeneous. Stirring was not employed. Each fusion was allowed to cool slowly. When the temperature had dropped to about 100° above the solidification point expected for the mixture, temperature readings were taken every three minutes until solidification of the material was complete. Temperature readings (millivolt readings of the potentiometer converted to Centigrade degrees) were made by means of a platinum-platinum (10) rhodium thermocouple which had been calibrated according to the recommendations of Roeser and Wensel (7). The mullite or silica protection tube for the thermocouple dipped into the melt to a depth of about 2 in. From the data, cooling curves of both the direct type (temperature vs. time) and of the inverse rate type (temperature vs. time required for the melt to fall through a definite temperature interval) were plotted.

Cooling curves could not be duplicated exactly for either the same sample or for separate samples of the same composition. This caused us to suspect a change in composition because of (*a*) interaction of the components and subsequent loss of a volatile reaction product, and (*b*) volatilization of unreacted material. A series of weight-loss-on-heating experiments on the single compounds were carried out and it was found that volatilization for each was of the order 0.5% for a 3-hr heating period. However, the weight loss due to volatilization was appreciable (as high as 4% for a mixture consisting of 25% Bi_2O_3 and 75% eutectic) for mixtures of the components. It was found later that, except for the pastes, all other mixtures of Table I consisted of two liquid layers which could be observed easily through the sides of Vycor crucibles. Analysis of the layers, after cooling of the melts, varied even for mixtures of the same composition and regardless of whether the melts were quenched (by transferring the Vycor crucibles immediately to a cold air environment) or were allowed to cool slowly. The amount of Bi_2O_3 in all solvent-rich (large top layer) layers was less than 5%. The authors concluded, on the basis of the following facts, that chemical change had occurred in the melts: (*a*) variability of analytical data; (*b*) occasional escape of gas bubbles slowly from the melts at higher temperatures; and (*c*) the authors' observation that the molten mixtures (particularly those containing the eutectic) yielded larger quantities of smoke than the single components when molten. An indication of the nature of the reaction(s) will be given later in the discussion section of this paper. In spite of the fact that phase rule studies were terminated early because of the conclusion that chemical change had occurred in the molten mixtures, the authors now possessed some useful knowledge, in advance of the electrolysis studies, about the behavior of the mixtures at temperatures up to 950°C.

Electrical conductivity studies.—A dip-type cell designed by the authors of Vycor glass was used in measuring the electrical conductivity (at 1000 cycles only) of the mixtures. Briefly, the cell consisted of two vertical arms (of Vycor tubing 1.9 cm diameter and 10 cm long) which were joined horizontally by a 5-cm length of Vycor capillary tubing. The underside of the capillary, at the center, was slotted to permit entry of melt into the cell. A length of 8-mm Vycor tubing, extending vertically from the center of the upper side of the capillary, served as a handle for the cell. Platinum disk electrodes, welded to platinum leads, dipped into the vertical arms of the cell. The cell constant was determined by measuring the specific resistance of fused sodium chloride in this cell and then using that value together with the specific conductance values available in the literature (8).

It was observed that the conductances of the molten mixtures were never lower than 1.5 ohm^{-1} cm^{-1} [NaCl (8) is 4.05 ohm^{-1} cm^{-1} at 950°C]. The conductivity was observed to be independent of the depth of immersion of the platinum disk electrodes in the melt as long as the time interval between measurements was of the order 2 or 3 min. One can attribute this fact to the extremely small change in resistance. For time intervals longer than 2 or 3 min, fluctuations in conductivity were observed for the same mixture because of composition changes and not because of encountering two liquid layers. Aside from the fact that the studies furnished additional evidence for changes in composition, it was of interest to know that the melts were good conductors of the current.

Electrodeposition

In the electrolysis studies, mixtures containing 10% and 25% by weight of Bi_2O_3 in the NaCl-$CaCl_2$ eutectic or in NaCl or in $CaCl_2$ were employed. Various combinations of platinum, tungsten, graphite, and copper were used as electrodes. The cathode always rested on the bottom of the crucible containing the fusion, while the anode dipped sufficiently far enough into the fusion to make electrical contact. The distance between the electrodes was 4 cm. A copper coulometer placed in series with the electrolysis cell made it possible to calculate approximately the average current which passed through the cell during the period of electrolysis. Porcelain crucibles of 250-ml capacity proved to be more satisfactory than either clay, graphite, or Vycor crucibles as containers

TABLE I. *Electrodeposition of bismuth*

Solvent: $NaCl$-$CaCl_2$ eutectic mixture (mp, 505°C) 51.5 mole % NaCl and 48.5 mole % $CaCl_2$

Expt.	Wt of charge (g)	Bi_2O_3 (%)	Temp °C	Electrodes		Cell voltage	Ammeter (amp)	Cathode current density (amp/dm²)	Elapsed time (hr)	Metal recovered (g)	Rate of metal recovery (g/hr)	Product purity (% Bi)	Cathode current efficiency (%)
				Cathode	Anode								
1	258	25	800	W	Pt	5.7	5.1	204	1.50	12.1	8.1	88[a]	35[a]
2	346	25	800	W	Pt	4.5	5.0	198	1.23	15.3	12.4	98	95
3	345	25	800	W	Pt	7.5	4.7	184	1.40	8.9	6.4	99	52
4	269	10	600	C	Pt	8.5	5.0	46	1.62	Powder	—	—	—
5	269	10	600	W	C	7.5	2.5	22	2.06	Powder	—	—	—
6	368	10	600	W	C	5.5	4.0	39	1.65	Powder	—	—	—
7	345	10	600	W	C	6.3	4.0	39	2.12	11.2	5.3	94	51
8	359	10	600	W	C	8.2	4.0	39	1.55	4.5	2.9	98	28
9	334	10	600	W	C	9.1	4.5	44	2.00	2.3	1.2	98	10
10	294	0	600	W	C	7.4	4.0	40	1.92	Ca, CaC_2 traces	—	—	—
11	410	25	800	W	C	5.5	4.0	40	1.27	10.0	7.9	98	75
11a	375	25	800	W	C	2.7	4.0	39	1.20	9.6	8.0	97	76
12	392	25	800	Cu	C	6.9	4.0	160	1.38	10.2	7.4	89[b]	63[b]
13	383	25	800	Cu	C	2.0	4.0	160	1.48	18.4	12.4	75[b]	88[b]
14	397	25	800	W	C	4.8	2.1	21	2.10	13.1	6.2	98	113
15	347	25	800	W	C	9.1	2.0	21	2.10	12.6	6.0	96	115
16[c]	344	25	950	W	C	4.0	4.5	44	0.80	14.4	18.0	98	152
17[c]	361	25	950	W	C	3.9	2.3	19	0.58	6.0	10.3	97	172
18[d]	465	25	950	W	C	4.7	4.8	46	1.71	18.6	10.9	96	87
19[d]	479	25	950	W	C	4.6	5.0	49	0.92	49.1	53.0	98	410

[a] Based on actual Bi content; 11% Pt as impurity.

[b] Based on actual Bi content; copper impurity.

[c] $CaCl_2$ as solvent.

[d] NaCl as solvent.

for the mixtures. For a particular mixture, the heating time necessary to secure a two-layer melt (10% Bi_2O_3, small orange-red liquid layer on the bottom and a large yellow liquid layer on the top) or an apparently homogeneous paste (25% Bi_2O_3, yellow throughout) averaged approximately 50 min. At the end of that period, electrodes were inserted into the mixture and the electrolysis begun. The temperature of the furnace was maintained constant during the entire period of electrolysis. At the end of the electrolysis and after the crucible and contents were cool, the metal slug or button found on the bottom of the crucible was crushed until fine granules and powder resulted. The crushed material was then digested with a large volume of hot water for about 15 min, filtered, and dried at 100°C. Samples of the dried material were then analyzed for bismuth.

The bismuth was determined (9) by precipitating it as the phosphate, by means of 10% diammonium phosphate, from dilute nitric acid solution and finally igniting at 800°C. Tungsten, carbon, and platinum were present in very small amount as impurities largely because of the sparking which occurred occasionally around the electrodes during electrolysis. The "anode effect," generally observable in the electrolysis of molten materials, was present in most experiments of our research. However, in spite of the anode effect, current efficiencies were reasonably good. Electrolysis data appear in Table I.

Discussion

Interaction of the components.—There appear to be at least four reactions which involve the components even when a melt is not being electrolyzed. They are the following:

$$\mathrm{Bi_2O_3 + O_2 \rightarrow Bi_2O_5} \qquad (\mathrm{I})$$

$$\mathrm{Bi_2O_5 + 4NaCl \rightarrow Na_4Bi_2O_5 + 2Cl_2} \qquad (\mathrm{II}a)$$

$$\mathrm{Bi_2O_5 + 2CaCl_2 \rightarrow Ca_2Bi_2O_5 + 2Cl_2} \qquad (\mathrm{II}b)$$

$$\mathrm{2Bi_2O_3 + 3Cl_2 \rightarrow BiCl_3 + Bi_3O_2Cl_3 + 2O_2} \qquad (\mathrm{III})$$

$$\mathrm{BiCl_3 + 2NaCl \rightarrow Na_2BiCl_5} \qquad (\mathrm{IV}a)$$

$$\mathrm{BiCl_3 + CaCl_2 \rightarrow CaBiCl_5} \qquad (\mathrm{IV}b)$$

It is generally known that bismuth (V) oxide is formed when oxygen is passed over hot bismuth

(III) oxide. When bismuth trioxide was added to molten NaCl and/or $CaCl_2$ contained in a porcelain crucible in some of the authors' preliminary studies, a scarlet to reddish brown substance was formed on the surface of the melt. This substance sank slowly through the melt and the color persisted only until the mass had reached the bottom of the crucible. At the same time, there was the expulsion of a quantity of gas greater than that observable initially from the melt. The scarlet color, which is definitely characteristic of the higher oxide, led us to believe that bismuth (V) oxide had been formed. Thus, the first reaction is a logical one. Three facts support reaction (II), viz., (*A*) the gas which escaped from the mixture did contain chlorine; (*B*) the Kahlenbergs (10) have demonstrated quantitatively that tungsten oxide, a substance similar in some respects to bismuth (V) oxide, reacts with molten sodium chloride in the manner

($2WO_3 + 2NaCl \rightarrow Na_2O \cdot W_2O_5 + Cl_2$); and (*C*) Belladen (11) has shown the existence of lead pyrobismuthite, $2PbO \cdot Bi_2O_3$ or $Pb_2Bi_2O_5$, melting at 625°C. Reaction (III) is in keeping with the observation of others (12) that the trichloride, together with smaller amounts of an oxychloride ($Bi_3O_2Cl_3$), is formed by the action of chlorine on heated Bi_2O_3 or Bi_2O_5. The double chloride of reaction (IV) is quite analogous to the potassium pentachlorobismuthite, K_2BiCl_5, an amber-yellow solid which Aloy and Frébault (13) prepared by passing a current of chlorine and bismuth trichloride vapor over potassium chloride at red heat. Thus, the evidence cited lends considerable support to the four series of reactions which appear to be involved in the interaction of the components.

The electrolysis.—The data of Table I reveal that bismuth metal can be obtained easily by the electrolysis of mixtures of Bi_2O_3 and either the NaCl-$CaCl_2$ eutectic or the single salts. Platinum anodes were attacked severely because of a combination of conditions which were present during the electrolysis, such as the sparking which accompanied the anode effect together with the evolution of both oxygen and chlorine at the anode; consequently, the large-scale use of the metal in this particular electrolysis is economically unsound.

A tungsten cathode and carbon anode represent the best electrode combination employed in this work. Abnormally high current efficiencies, that is, values greater than 100% in some experiments, are attributable definitely to chemical reduction of bismuth compounds by fairly large pieces of graphite which became detached from the anode as a result of unusually severe sparking which accompanied the anode effect in those experiments. However, it is reasonable to assume that all current efficiencies would have run a little higher if there had not been partial short-circuiting of the electrodes through the walls of the porcelain crucible. Others (10) found this to have been true in their work.

From an academic point of view, it would be more desirable if the data showed definite relationships among the following variables: electrode combinations, cathode current density, cathode current efficiency, purity of deposit, and recoverable metal deposited in unit time. Such definite relationships do not exist for the cathode current densities which were employed in these studies. Despite the absence of such relationships in this work, the data are of preliminary interest from an industrial or commercial point of view. Conditions for obtaining bismuth metal electrolytically from melts, such as employed in this work, are not critical! All deposits were satisfactory except in experiments 12 and 13 where copper was used as cathode material. In those experiments, there was serious contamination by copper. However, if one were interested in obtaining an alloy of bismuth and copper, use of a copper cathode in melts of the type used in this work might be of value. Wide differences in cell voltages were perhaps due to the anode effect and to electrode polarizations and resistance changes of the electrolyte. Energy consumption values, based solely on the electrolysis and not on the furnace requirements, calculated for experiments 11 and 11*a* are, respectively, 1.275 and 0.614 kwhr/lb of bismuth. The rating of the crucible furnace used in this work was 6 kw at 63 volts. The authors believe that energy consumption values calculated for the two experiments would compare favorably with industrial electrolytic processes for many different metals. Work, now in progress, is being carried out with a view toward ascertaining more completely the applicability of the process to the large-scale production of bismuth metal. Ores will be studied. It is very likely that some impurities from the ores may codeposit with the bismuth metal; however, it should be possible to remove such impurities easily by an electrorefining process.

What can one say concerning the reaction(s) by which bismuth metal was formed in the research? Actually, both chemical and electrochemical processes were involved. Consider the following processes: (*a*) cathodic discharge of trivalent bismuth ion present in the melts; (*b*) cathodic discharge of sodium or calcium as the metal and subsequent interaction of the metal and bismuth (III) oxide to yield metallic bismuth; and (*c*) anodic oxidation of $Bi_2O_5^{-4}$ ion [cf. equations (II*a*) and (II*b*)] to bismuth (V) oxide and reduction of the latter by fragments of the carbon anode to metallic bismuth.

The sources of trivalent bismuth ions in the melt would be both $BiCl_3$ [cf. equation (III)] and unreacted Bi_2O_3. According to Mellor (14), electrolysis of the oxide has been detected at 200° even though the oxide melts in the vicinity of 800°C. If such is the case, then the oxide in the melts should contain the trivalent bismuth ion. Discharge of bismuth ion, Bi^{+3}, [process (*a*)] should, under normal conditions, be easy in view of the fact that the metal is still considerably more noble than either sodium or calcium in melts, just as is true for aqueous solutions. Process (*b*) cannot be excluded as a possibility when one considers the fact that the electrolyzing voltages were, in all experiments except one, higher by at least one volt than the decomposition voltages which have been obtained by others for both salts from a study of their current-potential curves. Kortüm and Bockris (15) give the following decomposition voltages: NaCl, 3.06 volts at 800°C and $CaCl_2$, 3.23 volts at 852°C. Another consideration in support of the process as a possible one is that cathodic discharge of either sodium or calcium would involve the decomposition voltage(s) of the original salt(s) and/or the pyrobismuthite and pentachlorobismuthite formed by interaction of the components. For any one of the salts, the decomposition voltage might conceivably be less than 2.7 volts if its measurement involved using a carbon anode and tungsten cathode. It has been reported [Reference (15), p. 477] that decomposition potentials of cryolite-alumina melts, at low current densities, are 2.10 volts with a platinum anode and 0.98 volt with carbon. However, complete justification for process (*b*) would require a determination of decomposition voltages for the pure salts under the conditions of this work and cathode potentials for the electrodeposition of bismuth under the same conditions. Evidence for process (*c*) is not readily available.

Thermodynamic calculation of decomposition voltages for the melts and for various electrode combinations would require the making of an extensive number of fundamental assumptions. However, the number of such assumptions could be reduced considerably if one were to make a kinetic study of the slight interaction which takes place between the components of the mixtures.

SUMMARY

1. Bismuth metal of high purity can be obtained by the electrolysis of molten mixtures of Bi_2O_3 (10% and 25%) and either the NaCl-$CaCl_2$ eutectic mixture or the single salts.

2. Conditions for electrodeposition of bismuth from such melts are not critical in spite of the fact that slight interaction does occur between the components of the melts.

3. A tungsten cathode and carbon anode appear to be the best electrode combination employed in the work.

4. A discussion is given of the nature of the interaction between the components of the mixtures and the reactions by which the bismuth metal was formed.

5. Results reported herein are sufficiently encouraging to warrant research now in progress to ascertain more completely the applicability of the process to the large-scale production of bismuth metal from ores.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1955 issue of the JOURNAL.

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Mechanism of the Reaction of Hydrogen with Zirconium

I. Role of Oxide Films, Pretreatments, and Occluded Gases[1]

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ABSTRACT

Previous studies have shown the reaction of zirconium with hydrogen to be sensitive to surface preparation, surface films, heat treating cycles, cold working of the metal, and nonmetallic impurities.

Experiments were made on the rate of reaction of high purity zirconium with pure hydrogen using a sensitive microbalance method, and an all glass and ceramic vacuum system to minimize contamination.

The effect of a preliminary vacuum heating cycle on rate of reaction with hydrogen at 150°C was studied by varying the temperature of the vacuum heating cycle from 150° to 700°C. Samples having the room temperature oxide present showed only a slow rate of reaction, while samples heated to 700°C for one hour showed a rate of reaction 7700 times as great. Results also showed that the oxide film was effectively removed by heating in a vacuum for one hour at 500°C.

A study was made of the thickness and nature of the oxide film. Thus, the film formed in air at room temperature was more resistant to hydrogen attack than thicker oxides formed at higher temperatures. Studies on the effect of small quantities of oxygen and nitrogen in solid solution indicate only minor effects. Results suggest that considerable revision is necessary in concepts of the mechanism of the hydrogen reaction on metals.

INTRODUCTION

Occlusion of hydrogen by metals has been the subject of a large number of scientific studies (1); however, comparatively minor attention has been given to the question of rate of reaction. Unfortunately, many experimental studies on exothermic occluders such as zirconium appear to have been made under poorly defined experimental conditions and conclusions drawn from inadequate data. Therefore, the mechanism of occlusion has been found to be complicated, and the influence of surface preparation, cold working of the metal, occluded gases, hydrogen pretreatment, oxide films, and composition of the gas atmosphere is not understood.

A simple physical chemical analysis of the rate of occlusion would show that a number of separate processes are involved for metals such as zirconium. These are: first, preliminary processes at the surface, including chemisorption of the molecule and subsequent splitting apart of the molecule into atoms or ions; second, diffusion of hydrogen atoms, ions, or molecules through the oxide or other surface film; third, transfer at the metal-oxide interface of the hydrogen molecule, atom, or ion from the oxide into the metal; fourth, diffusion of hydrogen along grain boundaries or through the metal lattice; fifth, formation and growth of one or more hydride phases.

From an experimental point of view, it is difficult to separate the rate-controlling process from the other rate processes. This is especially true for zirconium where two phases may exist. In addition, stable oxide films and other contaminating films form readily on the metal surface, and these may retard reaction with hydrogen. These films may dissolve in the metal at higher temperatures under vacuum or inert gas atmospheres and reappear if the rate of film formation is greater than the rate of solution of the oxide into the metal. Therefore, it has been difficult to study the relative influence of oxide films and the physical structure of the metal, and many unusual physical effects have been noticed for this reaction.

Occlusion of hydrogen by zirconium has been reviewed by Smith (1). De Boer and Fast (2) and Hägg (3) have studied the solubility of hydrogen and find that at room temperature the solubility corresponds to $ZrH_{1.95}$. Desorption occurred on lowering the pressure. Hydrogen was stated to be more soluble in the β-form, and the transition between α and β forms occurs at 865°C. Hall, Martin, and Rees (4) have studied the solubility of hydrogen in zirconium and zirconium-oxygen solid solutions at temperatures up to 1000°C and at pressures of 1–760 mm of Hg. Special care was used to remove the contaminating influence of oxide and other films. These authors suggested that much of the disagreement on the temperature at which hydrogen reacts with zirconium was due to poor experimental techniques and the

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presence of surface films. The effect of oxygen on occlusion capacity showed that oxygen diminishes the quantity of hydrogen taken up by a volume equivalent to the oxygen solution.

Crystal structures of the hydrogen-zirconium system have been studied by Hägg (3). Four hydride phases were observed. Hydrogen was adsorbed up to 5 atom % in the hexagonal close-packed lattice without an appreciable change in lattice parameters. An expansion of 15.4% occurs in zirconium for a hydrogen pickup corresponding to H/Zr = 1.92 (5).

Gulbransen and Andrew have studied the rate of reaction of hydrogen with zirconium specimens containing room temperature oxide film (6). Very little reaction occurred at 200°C while a more rapid reaction was found at 300°C. The effect of pressure on rate of reaction followed a square root relationship. The reaction was found to be very sensitive to pretreatment and surface films. A similar square root of pressure relationship was found for the rate of flow of hydrogen through Zr at temperatures between 375° and 920°C by Bernstein and Cubicciotti (7).

In this work the role of oxide films, pretreatments, and occluded gases on the rate of reaction of hydrogen with zirconium was studied.

Interpretation of the nature of the Occlusion Process

Theories on the variable rate of reaction.—An analysis of literature on the occlusion process for exothermic occluders such as zirconium indicates that two theories exist for the variable rate of reaction observed when zirconium is exposed to hydrogen. The first is the "rift theory" of occlusion developed by Smith (1). In this theory an expanding and contracting series of rifts are used to explain active and passive states of the metal. The second is the oxide film theory in which a coherent thin oxide film prevents access of hydrogen to the metal. However, this oxide dissolves in the metal at high temperature under high vacuo conditions. Clean metal is then exposed for reaction. The most recent work supporting this point of view is that of Hall, Martin, and Rees (4).

Before presenting the authors' work, it is of interest to indicate the main experimental characteristics of the occlusion process upon which Smith has developed the rift theory of occlusion. It should be noted that much of the work was made on specimens probably contaminated with oxide and other films.

Smith's characteristics of the occlusion process.—(*A*) Metal is inert to gaseous hydrogen at room temperature and normal pressure in its ordinary form. (*B*) If gradually heated the metal begins to react at an indefinite opening temperature. (*C*) The rate of reaction is self-accelerating in its early stages. (*D*) At high pressures the metal in its ordinary state reacts and is permeable at lower pressures. (*E*) Metal in its ordinary state reacts with hydrogen liberated upon it by chemical displacement or by electrolysis. (*F*) Permeability of metal to hydrogen may be increased or decreased by repeated absorption and evolution of hydrogen, apparently depending upon the rate with which the gas is expelled. (*G*) Metal heated to high temperatures in vacuo is inert to gaseous hydrogen and may be impervious to cathodic hydrogen. (*H*) Permeability is increased by plastic deformation, in some cases manyfold. This increase is accompanied by an increase in occlusive capacity.

In addition to these general characteristics Smith gives five additional characteristics of exothermic occluders such as zirconium. (*I*) After a metal is heated to an activation temperature above that described in (*B*), the metal possesses for some time an induced high permeability at ordinary temperatures and pressures. This is known as thermal activation. (*J*) This high permeability declines gradually at a rate which differs from one lot of metal to another. (*K*) Metal having high permeability and charged with hydrogen loses its permeability slower than if uncharged. (*L*) If heated and cooled while charged with hydrogen, the metal shows decreased permeability and does not give up its hydrogen to vacuum until heated to above its opening temperature. (*M*) In the composition range of two solid phases, exothermic occluders show smaller permeability and occlusion capacity during absorption than during evolution of hydrogen. This phenomena is called hysteresis.

It is, of course, impossible to test all of these characteristics in one paper. However, results obtained in this work should be related in each case to the characteristics given by Smith and checked with the two theories of occlusion.

EXPERIMENTAL

A vacuum microbalance was used for all measurements (8). The 0.0127 cm thick specimens had surface areas of about 10 cm^2 and weighed 0.500 gram. Sensitivity of the balance was 1 division (0.001 cm) per microgram, and weight change was estimated to ¼ of a division (0.25×10^{-6} gram). A mullite furnace tube was used to contain the specimen and was sealed directly to the Pyrex apparatus. The vacuum system, behavior of which has been studied previously (9), was of all glass construction and could be evacuated readily to pressures considerably lower than 10^{-6} mm of Hg.

Pure hydrogen was prepared by diffusing purified electrolytic hydrogen through a palladium tube (10). A special gas train was used for preparing pure oxygen. Reagent grade nitrogen was used for preparing zirconium specimens with given nitrogen contents.

Two sources of high purity iodide zirconium were

TABLE I. *Analyses of zirconium samples*

	(W) APD Zr		Foote Zr
	Spec. %	Chem. %	Typical
Si	0.002–0.007		0.01
Fe	0.037–0.049	.01	0.04
Al	0.0027–0.0037		0.01
Cu	(0.0005–0.0030)		<0.01
Ti	0.002–0.003		0.03
Mn	0.005		<0.001
Ca			0.01
Mg	(0.001)		<0.003
Pb	(0.0025)		<0.001
Mo	(0.001)		<0.001
Ni	0.0025–0.004		0.01
Cr	0.001–0.0018	.003	0.001
Sn	< (0.001)		0.001
W	0.010		<0.001
N		.001–.0025	<0.01
O		(.020)	<0.01
H		(.002)	<0.02
C		(.010)	<0.001
Hf			2.40

( ) Outside limits or isolated values.

used. The first[2] contained 2.4% hafnium, and the second[3] was a hafnium-free zirconium. Spectrographic and chemical analyses are given in Table I.

All specimens used had previously been abraded starting with 0 and finishing with 4/0 emery paper. The last two papers were used under purified kerosene. Samples were then cleaned successively with soap and water, distilled water, petroleum ether, and absolute alcohol. After a preliminary weighing, specimens were placed in a desiccator until ready for use. Chemically polished specimens were dipped in a solution of 40 cc nitric acid, 40 cc water, and 10 cc hydrofluoric acid.

RESULTS AND DISCUSSION

To study the rate of hydriding of zirconium it was necessary to devise a test procedure which gave a reaction rate characteristic of an oxide-free metal and a reaction rate which was reproducible. Since the oxide film normally present on the surface cannot be reduced in the case of zirconium oxides, it was necessary to remove the oxide by heating in high vacuo. It was found that heating the specimen to 700°C in a vacuum of 10^{-6} mm or less for one hour gave a reproducible reaction rate with hydrogen. For convenience the conditions of 150°C and a pressure of 2.4 cm of Hg were chosen. The reaction showed no evidence of an induction period.

Results are given in terms of weight gain in micrograms/cm² and plots are made of weight vs. time in minutes.

Effect of temperature of vacuum heating.—To show the effect of vacuum heating procedures on rate of hydriding at test conditions, specimens were heated for 1 hr at a series of temperatures in high vacuo before cooling to 150°C to determine the rate of hydriding. If it is assumed that the rate of reaction with hydrogen at low temperatures was limited by the presence of oxide films, vacuum heating at higher temperatures, which tends to dissolve the oxide, should increase the rate of reaction. In experiments presented here vacuum heating was made in the same apparatus as the rate study and without intermediate exposure to a gas atmosphere of any kind.

Fig. 1 and 2 show the results. A new specimen was used for each experiment. Curve A in Fig. 1 was the reaction of a specimen having the room temperature equilibrium film, while curve B shows the rate of attack after a preheat of one hour at 150°C. Curves A, B, and C of Fig. 2 show the rate of attack with hydrogen after preheats of one hour at 300°, 500°, and 700°C. It was found that the 500° and 700° experiments gave similar rates of attack. Curves B and C were typical of many tests for these conditions of

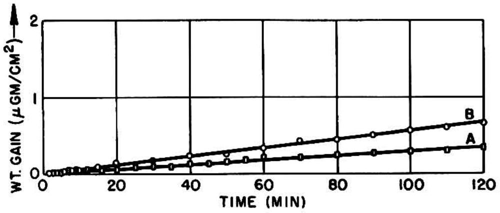

FIG. 1. Effect of time and temperature of heating on hydriding of Zr at 150°C, 2.4 cm of Hg of H_2. Curve A—room temperature equilibrium film; curve B—preheated 150°C, 1 hr.

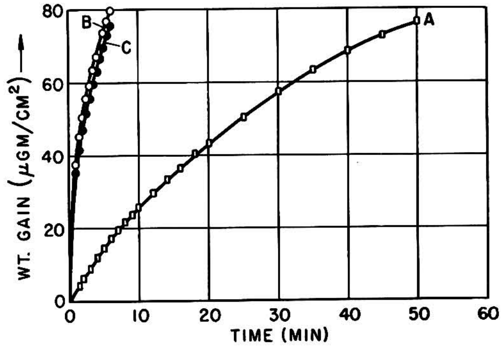

FIG. 2. Effect of temperature of heating on hydriding of Zr at 150°C, 2.4 cm of Hg of H_2. Curve A—preheated 300°C, 1 hr; curve B—preheated 500°C, 1 hr; curve C—preheated 700°C, 1 hr.

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[2] Prepared by the Foote Mineral Company.

[3] Made by the Westinghouse Atomic Power Division and secured through the courtesy of the Atomic Energy Commission.

pressure and temperature. Results were reproducible within the limits of experimental error.

The rate of reaction for curve A of Fig. 1 was zero for the first 5 min and averages 0.473×10^{-4} $\mu g/cm^2/sec$ for the first 2 hr. Curve C of Fig. 2 shows a rate of reaction of 0.365 $\mu g/cm^2/sec$ for the first 2 min. The ratio of the rate of reaction of specimens having the room temperature oxide present to the specimen annealed at 700°C was 1/7700. An even greater ratio would be found if the rates were calculated for the one-minute time interval.

Results can be interpreted readily by the oxide film theory. Thus, the inert character of the metal in its ordinary state can be attributed to the normal room temperature oxide film having a thickness of the order of 10 to 50 Å. This film is transparent and is an effective barrier to diffusion of gaseous hydrogen. It dissolved gradually into the zirconium as the temperature of heating was raised and the rate of reaction, therefore, was greatly increased. There appears to be no evidence that high heating of a metal such as zirconium renders it inert as interpreted by Smith (1).

Effect of thickness and character of oxide films on rate of reaction.—Fig. 3 shows weight gain vs. time curves for a series of oxide pretreatments in which the thickness and character of the oxide was studied. Curve A shows the weight gain curve for the specimen containing the room temperature equilibrium oxide. Curve B shows the rate of reaction for a specimen having been preheated under high vacuo to 700°C for one hour and then exposed to 0.1 atm pressure of oxygen at 25°C for 20 hr. Curve C shows the rate of reaction for a specimen which had been annealed at 700°C and then oxidized at 150°C at an oxygen pressure of 7.6 cm Hg for 5 min to form an oxide film 63 Å thick. Curves D and E show the effect of oxide films of 500 Å thickness formed at 250° and 275°C, while curve F shows the rate of reaction of a film-free specimen.

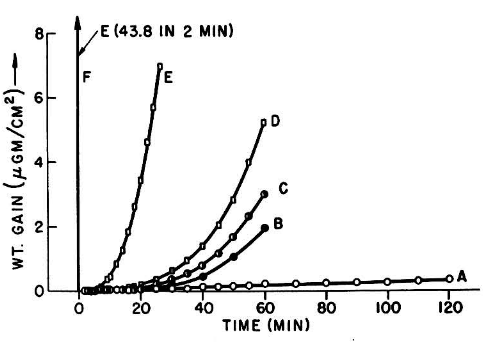

FIG. 3. Effect of oxide on hydriding of Zr, 150°C, 2.4 cm H_2. Curve A—room temperature equilibrium film; curve B—preheated +20-hr exposure to O_2 at room temperature; curve C—preheated +63 Å film at 150°C; curve D—preheated +500 Å film at 250°C; curve E—preheated +500 Å film at 275°C; curve F—preheated, no film.

These results again may be explained on the basis of a coherent oxide film which dissolves slowly in the metal at temperatures of 250°C and higher. In general, oxides formed at room temperature have the greatest effects on rate of hydriding. The thicker films formed at temperatures of 250° and 275°C are less resistant to hydriding for two reasons. First, solution of the film occurs which diminishes the film thickness. Second, the oxides formed at higher temperatures have a larger crystallite size. Thus, the fitting of the grains of oxide may be less perfect, and a greater porosity would be noted.

The fact that rate of reaction increases with time can be attributed to gradual breakdown of the oxide film physically by passage of hydrogen as well as to the gradual solution of the oxide into the metal.

Again the oxide film theory appears to explain observed facts better than the rift theory.

Comparison of source of zirconium.—Fig. 4 and 5 show a comparison of reaction rates for two sources of zirconium.[2, 3] Fig. 4 shows comparison of the rate of reaction of the two specimens having the room

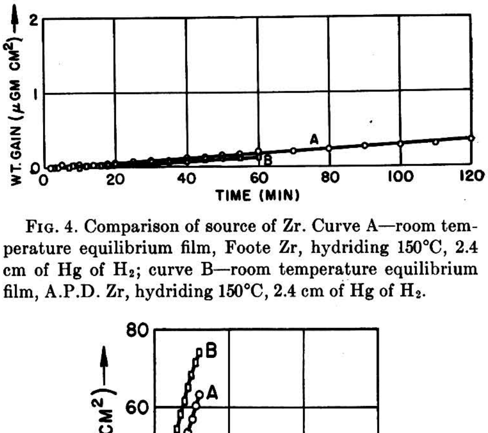

FIG. 4. Comparison of source of Zr. Curve A—room temperature equilibrium film, Foote Zr, hydriding 150°C, 2.4 cm of Hg of H_2; curve B—room temperature equilibrium film, A.P.D. Zr, hydriding 150°C, 2.4 cm of Hg of H_2.

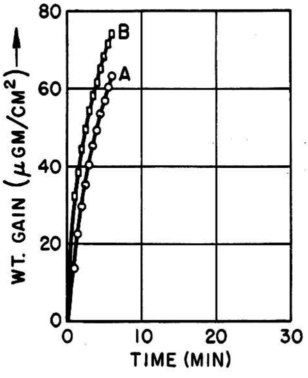

FIG. 5. Comparison of source of Zr. Curve A—Foote Zr, preheated 1 hr, 700°C, hydrided 150°C, 2.4 cm of Hg of H_2; curve B—A.P.D. Zr, preheated 1 hr, 700°C, hydrided 150°C, 2.4 cm of Hg of H_2.

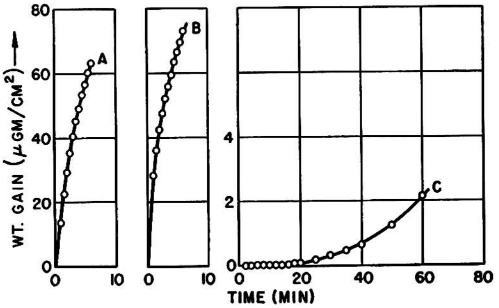

FIG. 6. Effect of pretreatment on hydriding Zr 150°C, 2.4 cm of Hg of H_2. Curve A—preheated 700°C, 1 hr; curve B—preheated-hydrided 150°C, heat up 700°C; curve C—preheated-hydrided 150°C, heat up 700°C, room temperature oxidation.

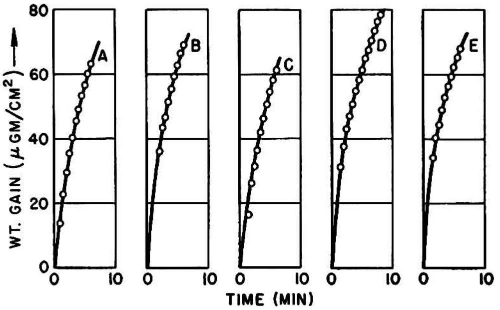

FIG. 7. Effect of dissolved oxygen on hydriding of Zr 150°C, 2.4 cm of Hg of H_2. Curve A—700°C preheated 1 hr; curve B—0.016% O_2 added, preheated 1 hr; curve C—0.027% O_2 added, preheated 1 hr; curve D—0.064% O_2, preheated 1 hr; curve E—0.0679% O_2 added, preheated 1 hr.

temperature equilibrium oxide film present, while Fig. 5 shows a similar comparison for the 700°C annealed specimens. Agreement between results for the two sources of zirconium was good.

Effect of successive hydrogen treatments and exposure to O_2.—Smith (1) has stated that successive hydrogen treatments affect permeability and occlusive capacity of the metal. In early stages of the reaction up to a H/Zr ratio of 0.2, no such evidence was observed providing one is working with an oxide-free zirconium surface.

Three rates of hydriding experiments were compared in Fig. 6. Curve A shows the control experiment with the rate of hydriding determined after the 700°C vacuum anneal. Curve B shows a rate of hydriding experiment for a sample which was given a high vacuo anneal at 700°C, hydrided at 150°C to 100 μg/cm^2 or to $ZrH_{0.2}$, the hydrogen removed by heating to 700°C then cooled to 150°C for the second hydriding. Curve A shows a total reaction of 57 μg/cm^2 for 5 min while Curve B shows a total reaction of 66.5 μg/cm^2 for 5 min. A small change appears in the rate of reaction due to previous adsorption and desorption of hydrogen in the lattice. However, the effect is a minor one when compared to the effect of oxide films. This is shown in curve C of Fig. 6. In this experiment the sample was heated, hydrided at 150°C, heated to 700°C, exposed to room temperature oxygen, then hydrided at 150°C. The effect of room temperature oxidation was great.

More experiments will have to be made to determine effect of the reaction of large quantities of hydrogen and subsequent removal on the rate of hydriding. Small quantities adsorbed and removed have only minor effects on the rate of hydriding.

Effect of oxygen in solid solution.—Samples of zirconium were heated to 700°C to dissolve the oxide film, then dosed with oxygen to give samples having 0.16, 0.027, 0.064, and 0.068 weight per cents of oxygen above the oxygen content of the original metal. Specimens were then heated in vacuo for 1 hr at 700°C to homogenize the oxygen before cooling to 150°C where further reaction with hydrogen occurred. Rapid homogenization was assumed to occur in the one-hour vacuum anneal at 700°C for the following reasons: (*a*) thickness of the specimens was only 0.0127 cm with both sides of the specimen exposed to the original oxygen treatment; (*b*) the small amounts of oxygen that had to be homogenized; (*c*) the high rate of attack of zirconium with oxygen at 700°C.

Results are shown in Fig. 7. The curves show total weight gain values varying from 55 μg/cm^2 to 63 μg/cm^2 after 5 min of reaction. Within experimental error, oxygen in solid solution in small amounts exerts only minor effects on the rate of hydriding at 150°C.

Effect of nitrogen in solid solution.—Samples of zirconium were prepared as described above except that reagent grade nitrogen gas was used to dose the

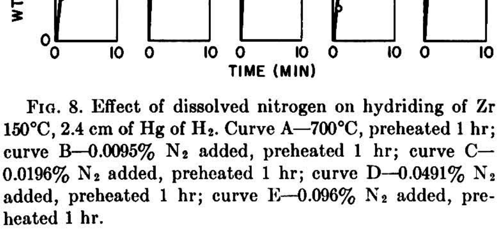

FIG. 8. Effect of dissolved nitrogen on hydriding of Zr 150°C, 2.4 cm of Hg of H_2. Curve A—700°C, preheated 1 hr; curve B—0.0095% N_2 added, preheated 1 hr; curve C—0.0196% N_2 added, preheated 1 hr; curve D—0.0491% N_2 added, preheated 1 hr; curve E—0.096% N_2 added, preheated 1 hr.

samples with given amounts of nitrogen. Thus, samples having 0.0095, 0.0196, 0.0491, and 0.096 weight per cent of nitrogen above the original nitrogen content were prepared. Again homogenization was assumed to occur in a one-hour vacuum treatment at 700°C for reasons given above. Results are shown in Fig. 8. As in the case of oxygen in solid solution, the curves show that small amounts of nitrogen have only minor effects on the rate of reaction.

SUMMARY AND CONCLUSIONS

High purity zirconium containing the room temperature equilibrium oxide film reacts very slowly with hydrogen at 150°C and 2.4 cm of Hg pressure, and in a self-accelerating manner. Similar specimens preheated in high vacuo at temperatures above 500°C for one hour react very rapidly with hydrogen at 150°C and 2.4 cm of Hg pressure without an induction period. The ratio of the rate of reaction for the preheated specimens relative to those not preheated was 7700 or greater.

Results were interpreted in terms of an oxide film limiting the rate of reaction, this film dissolving in the metal as the temperature of annealing was raised. Thus the oxide film present on the unannealed specimen limits the rate of reaction and imposes an induction period on the reaction.

Previous work summarized by Smith, showing that vacuum heating the metal decreases the rate of reaction of hydrogen, may be interpreted now as due to formation of an oxide or other contaminating film.

Further experiments show that the nature of the oxide film was very important in its resistance to hydrogen. Thus, room temperature equilibrium oxide films were more resistant to hydrogen than thicker oxide films formed at higher temperatures. This was explained in part by a partial solution of the oxide and to the presence of larger oxide crystallites in the films formed at higher temperatures.

Small amounts of dissolved oxygen and nitrogen up to 0.1 weight per cent have only a minor effect on the rate of hydriding at 150°C.

Successive hydrogen treatments show only minor effects on the rate of hydriding for hydrogen adsorptions up to 0.2 atom of H per atom of Zr.

Many of the unusual occlusive characteristics given by Smith may be interpreted on the basis of the oxide film theory which offers an effective resistance to the reaction with hydrogen at low temperatures.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1955 issue of the JOURNAL.

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Electrical Properties of Semiconducting AlSb[1]

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ABSTRACT

Measurements of some of the electrical properties of the compound AlSb indicate semiconducting characteristics comparable with those reported for silicon. Data were taken on the electrical resistivity, thermoelectric power, and Hall voltage as a function of temperature over the range from 80° to 1200°K. The energy band separation, as determined from the temperature dependence of the conductivity, is 1.5 to 1.6 ev. Mobilities of electrons and holes are approximately equal and are greater than 100 cm²/volt-sec at room temperature. Rectification characteristics are given for both *P*- and *N*-type samples of various resistivities. Both photovoltaic and photodiode effects were observed.

INTRODUCTION

During the past decade, much effort has been applied to the preparation and investigation of semiconducting properties of such elements as silicon, germanium, selenium, and tellurium. The object of this research has been not only to develop useful devices such as transistors and rectifiers, but also to interpret the properties of these elements in terms of modern theories of solids. Such extension of our knowledge concerning these fundamental processes is obviously of value whether one is interested in improving the characteristics of existing components, in developing new devices, or in the discovery and evaluation of new semiconducting materials. Electronic-device development has, in fact, proceeded to such a stage that a great variety of materials having special semiconducting characteristics are desired. To be more specific, in certain applications a high mobility of the charge carriers is of prime importance. Of the elements in common use at the present time, germanium exhibits the highest mobility. On the other hand, many applications require concentrations of minority carriers to be small over the temperature range of operation. Hence, the energy separation between filled and conduction bands must be sufficiently large so that the intrinsic contribution to the conductivity is negligible. Since this energy gap in silicon is approximately 1.1 ev as compared to 0.72 ev in germanium, it is understandable why extensive work is now being done on silicon for use in high temperature rectifiers and transistors.

In addition to elements such as those discussed above, a number of compounds have semiconducting properties. Several well-known examples of these are lead sulfide, cadmium sulfide, and cuprous oxide. Many other binary compounds which are semiconductors are known. In particular, it has been noticed that a large number of elements combine with antimony to form useful semiconducting materials. For example, with elements in Column I of the periodic table, such as Cs, Rb, and K, antimony combines to give compounds, such as Cs_3Sb, which find extensive use in photoemissive cells. From Column II, one obtains Mg_3Sb_2, whose semiconducting properties have been studied in detail by Boltaks (1), Zhuse (2), and others. The other series of elements in Column II yield materials of lower intrinsic resistivity, such as ZnSb and CdSb. The properties of these compounds have been studied by Telkes (3), and by Justi and Lautz (4). Elements of Column VI, when combined to form the compounds Sb_2S_3 (5), Sb_2Se_3 (6), and Sb_2Te_3, are also known to exhibit semiconducting properties.

Antimony also forms compounds with elements of the third column of the periodic table, that is, with aluminum, gallium, and indium. These compounds are especially interesting since they possess the zincblende crystal structure. At the initiation of the present investigations, there was no information available on the electrical properties of these compounds. Recently, however, a publication by Welker has appeared (7). Welker contrasts the structural and electrical characteristics known for the elements diamond, silicon, germanium, and gray tin of the fourth column of the periodic table with those expected for the general series of compounds composed of elements from the third and fifth columns. Specifically, these compounds are AlSb, InSb, GaSb, AlAs, InAs, GaAs, AlP, InP, and GaP.

PHASE DIAGRAM AND CRYSTAL STRUCTURE

Equilibrium studies of the aluminum-antimony system were carried out by Gautier (8) over fifty years ago. He noted that a high melting point was associated with the composition in which an equal

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[1] Manuscript received April 13, 1953. This paper was prepared for delivery before the New York Meeting, April 12 to 16, 1953.

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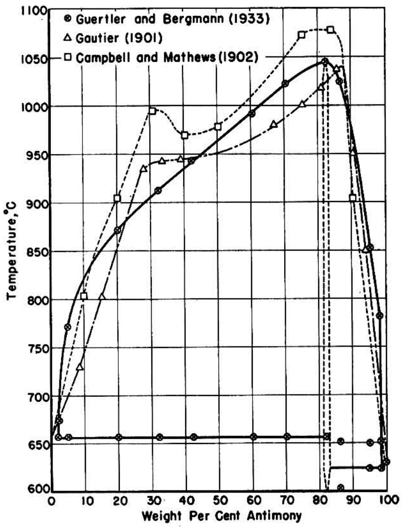
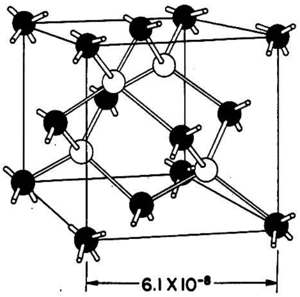


FIG. 1. Phase diagram of the aluminum-antimony system.



Face-Centered Cubic Diamond Structure	Lattice Constant
Diamond	3.5597×10^{-8} cm
Silicon	5.431
Germanium	5.657
AlSb	6.1361 ± 0.0003

FIG. 2. Crystal structure of the compound AlSb

number of aluminum and antimony atoms are present. Subsequent investigations were carried out by Campbell and Mathews (9), and by Tammann (10). It was not until 1933, however, that the currently accepted phase diagram was published by Guertler and Bergmann (11). Results of these investigations are summarized in Fig. 1.

It will be noted that the compound AlSb has a melting point of 1050°C as compared with melting points of 660° and 630°C for aluminum and antimony, respectively.

X-ray studies by Owen and Preston (12) in 1924 indicated that the intermetallic compound AlSb had the zincblende structure with a lattice constant of 6.126 Å. Recent x-ray studies at Battelle confirm the structure type and are in agreement with the reported lattice constant. These measurements indicate a lattice constant of $6.1361 \pm 0.0003 \times 10^{-8}$ cm as compared with the Owen and Preston value which, when converted from *kx* units, is 6.138×10^{-8} cm.

The structure of a unit cell of AlSb is shown in Fig. 2. Atoms of one element may be pictured as defining a face-centered cubic arrangement, while those of the second element define a similar configuration which interpenetrates the first. Hence, a total of 8 atoms—4 Al and 4 Sb—are contained in the unit cell. Each antimony atom has 4 aluminum atoms as nearest neighbors, at a distance of 2.657×10^{-8} cm. They are connected by a two-electron homopolar bond.

It is to be noted that the AlSb structure and bonding are similar to those of germanium and silicon. These semiconducting elements possess the diamond structure, a crystal form to which that of AlSb would reduce if both atoms were identical. The lattice constants of diamond, silicon, germanium, and AlSb are also given in Fig. 2.

RESISTIVITY AND ASSOCIATED PROPERTIES

Electrical resistivity, thermoelectric power, and Hall measurements were made over a temperature range from 80°K to 1200°K on a number of samples of aluminum antimonide containing different extrinsic carrier concentrations. The specimens, which were polycrystalline, were carefully annealed in order to reduce inhomogeneities in the samples, such as grain-boundary effects.

Specimens were measured, which showed resistivities ranging from 1×10^{-2} ohm-cm to 32 ohm-cm, at room temperature. These specimens had charge-carrier concentrations, determined from the Hall measurements, which ranged from 4×10^{19} to 1.5×10^{15} per cm^3. The specimen containing 1.5×10^{15} carriers/cm^3 has a resistivity of 32 ohm-cm at 25°C. Germanium with the same *P*-type carrier concentration would have a resistivity of around 2 ohm-cm.

Resistivity data are shown in Fig. 3. It was noted that the general shapes of the AlSb resistivity curves were remarkably similar to those of polycrystalline silicon containing boron impurities, except for the higher intrinsic slope in the case of AlSb. Resistivity data for silicon, as reported by Pearson and Bardeen (13), are consequently indicated by the dashed curves in Fig. 3. Carrier concentrations at room temperature as determined from the Hall measurements are shown for both AlSb and silicon specimens. Measurements presented in Fig. 3 were taken on *P*-type material, and mobilities of positive holes were computed from the resistivity and Hall data. The Hall coefficient as function of temperature for these specimens is shown in Fig. 4. Again, silicon curves from the data of

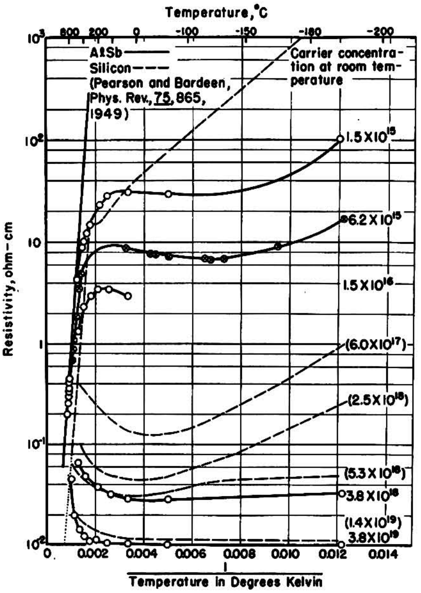


FIG. 3. Resistivity of AlSb as a function of temperature

Pearson and Bardeen are shown for comparison. Especially interesting is the fact that the Hall coefficient for AlSb begins to decrease at temperatures lower than those at which it decreases for silicon. This decrease is due primarily to the increase in the number of the minority N-type carriers from the filled band. Also, the sign of the Hall constant does not reverse in the intrinsic region. Both of these facts indicate that the ratio of the electron mobility to hole mobility in AlSb is nearly unity. Hence, the ratio of the effective mass of the electrons to that of the holes is also about one. In this respect, AlSb is different from silicon and germanium, where the effective mass of the electron is significantly less than that of the holes. For samples containing less than 10^{16} impurities/cm^3, lattice scattering predominates even at temperatures as low as 80°K, and the temperature dependence of the mobility approximates quite closely the $T^{-3/2}$ relationship. Magnitudes are very close to those reported for polycrystalline P-type silicon. In particular, room temperature mobility for the positive holes in AlSb was observed to be 100 cm^2/volt-sec. As was found in the case of silicon, it is to be expected that the crystallite boundaries might give a significant contribution to the resistivities measured on the polycrystalline specimens. Hence, the value given above can be considered only as a lower boundary. Values obtained for single crystals may be much larger. For ionized impurity concentrations greater than 10^{17}/cm^3, impurity scattering causes a reduction in the mobility at low temperatures. In fact, in the specimen containing 3.8×10^{19} carriers/cm^3, the mobility has been reduced, even at room temperature, to about 15 cm^2/volt-sec.

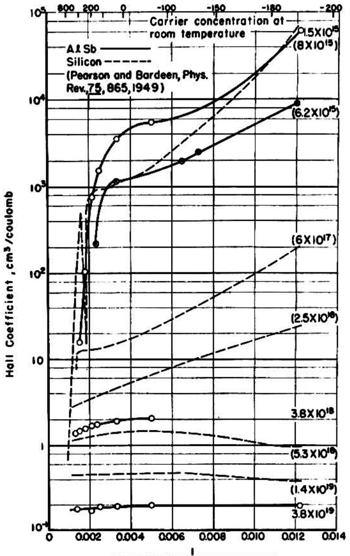


FIG. 4. Hall coefficient of AlSb as a function of temperature.

Another observation on an AlSb sample containing 1.5×10^{15} carriers/cm^3 was that the thermoelectric power changed from positive to negative at 275°C. In the sample with 6.2×10^{15} P-type carriers, the crossover temperature increased to approximately 500°C.

An approximate value of the energy-band separation in a semiconductor can be obtained from the slope of the log ρ vs. $1/T$ curve in the intrinsic region. Such a calculation gives a value of approximately 1.5 to 1.6 ev for AlSb.[3] This is somewhat larger than that of silicon, which is approximately 1.1 ev. A very important practical consideration is connected with the width of this forbidden band. This factor is important in determining the upper limit to the temperature at which a semiconductor device can be operated. For example, with germanium, having a band separation of 0.72 ev, the present upper limits of operation are 70°–80°C for most operations. With silicon, on the other hand, P-N junction diodes have been reported to operate at temperatures as high as 300°C.

RECTIFICATION AND PHOTOEFFECTS

When a metallic point contact is made with an impurity semiconductor as shown in Fig. 6 (lower

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[3] Note added in proof: Since the presentation of this paper, there has appeared a publication by H. WELKER in *Z. Naturforsch.*, **8a**, 248 (1953). His value of 1.65 ev for the energy-band separation in AlSb is in good agreement with the above result.

right corner), an asymmetric nonlinear current-voltage relationship is observed. If the semiconductor is P-type and the metal point is negative, a low resistance to the current is obtained, while for reversed polarities, a high resistance occurs. Such a device is called a P-type point-contact rectifier.

A number of specimens of AlSb were investigated for rectification and photoelectric phenomena. Rectification was found at point contacts of several different metals with polycrystalline AlSb specimens of various resistivities. Current-voltage characteristics for several such rectifiers are shown in Fig. 5. It will be noted that both P- and N-types of rectification were obtained. Although a number of different metals of widely varying work functions were used for the point contact, it was not possible to correlate observed rectification characteristics with differences in work functions. A somewhat similar situation has been reported by Meyerhof (14) in connection with silicon point-contact rectifiers.

Some rectifiers made from specimens containing P-N junctions exhibited saturation regions in their forward characteristics. In these cases, when the contact was moderately illuminated with white light, photoelectric effects were observed. Changes in forward current in the saturation region by as much as 100% were observed. The same contacts exhibited photo-emf's up to 25 mv. Similar observations have been reported for germanium by Benzer and others (15).

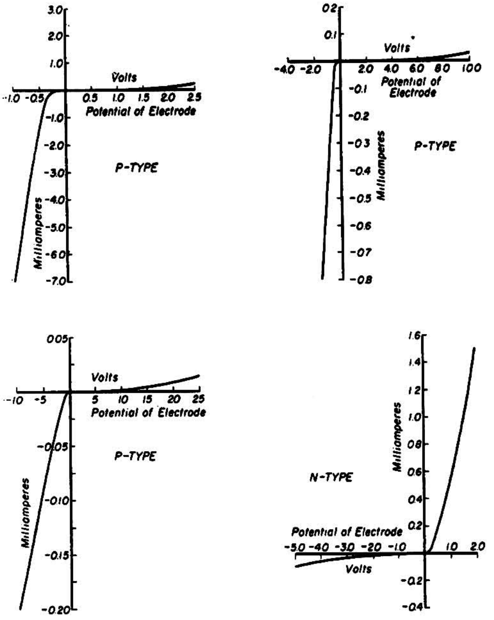

FIG. 5. D-C current vs. voltage characteristics for AlSb rectifiers.

Characteristics of AlSb point-contact rectifiers are compared in some detail with those of silicon rectifiers in Fig. 6 and 7. For this purpose, a more informative presentation of the current-voltage characteristics of semiconductor rectifiers is used. Fig. 6 shows the reverse and forward current variations with applied voltage of a P-type AlSb point-contact rectifier compared with those for Si rectifiers made from polycrystalline Si reported by Scaff and Ohl (16) in 1947. In addition to the similarity between the rectifiers, it will be noted that the rectification ratio at one volt for the AlSb rectifier, although slightly less than that for the Si, is about 800.

Fig. 7 shows characteristics for N-type AlSb point-contact rectifiers. These have been compared with the characteristics for improved point-contact silicon rectifiers reported by Ohl (17) in 1952. Improvement was obtained through bombardment by helium ions. It will be noted that the N-type AlSb rectifiers compare favorably with these silicon rectifiers. Rectification ratios as high as 10,000 at 4 volts are apparent. Although peak inverse voltages are low in the AlSb and the silicon rectifiers shown in the figure, higher peak inverse voltages can be obtained. For example, in other experiments, for which data are not presented in the figures, voltages

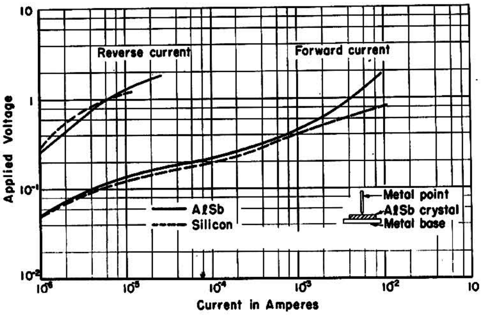

FIG. 6. Logarithmic plot of the d-c current vs. voltage characteristics for P-type AlSb and silicon.

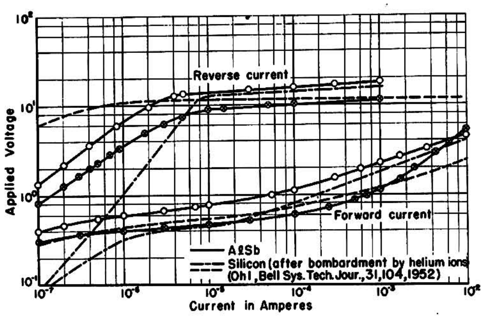

FIG. 7. Logarithmic plot of the d-c current vs. voltage characteristics for N-type AlSb and silicon.

as high as 90 volts were applied in the reverse direction without damage to the AlSb rectifiers.

CONCLUSIONS

In summary, this work has revealed that the compound AlSb can be considered as a new addition to the germanium and silicon family of semiconductors. Its structure is the diamond structure; its electrical properties vary with changes in amount of atomic imperfections in a manner strikingly similar to that of silicon. A wide range of electrical resistivities varying from 1×10^{-2} to greater than 30 ohm-cm has been achieved in homogeneous polycrystalline materials, and both *P*- and *N*-type electrical conductions were obtained. Outstanding differences between electrical properties of AlSb and Si appear to be the equivalence of electron and hole mobilities and the energy gap of 1.5 to 1.6 ev in AlSb as compared, respectively, with the 4 to 1 ratio and 1.1 ev gap for Si.

Also like Si, AlSb will make rectifying contacts with many different types of metal points. These rectifying contacts are characterized by low peak inverse voltages in the case of material with large carrier concentration, and higher peak inverse voltages in material with smaller charge-carrier concentrations. Further, preliminary evidence has been obtained to show that AlSb point-contact devices can be produced to act as electrical switches on exposure to light as well as used to convert light to electrical energy.

Appraisal of collected data on AlSb suggests that it may have advantages over Ge and perhaps Si for high temperature electronic-device applications of interest to the military. Its melting point being only 1050°C, whereas that of Si is 1420°C, indicates that procedures for processing AlSb may be more easily evolved than for Si.

Besides these advantages, the cost of high purity Al and Sb comparable in purity to the Ge and Si used as starting materials in rectifier and transistor manufacture is markedly smaller; for example, high purity Al and Sb cost less than \$5/lb as compared to \$300/lb for Ge and Si.

Based on these findings, it is apparent that further efforts to develop AlSb for use in place of Ge and Si in solid-state electronic devices should be rewarding.

ACKNOWLEDGMENTS

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1955 issue of the JOURNAL.

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Surface States of Cadmium Sulfide[1]

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ABSTRACT

Photoconductive and phosphorescent properties of cadmium sulfide are modified by adsorbed molecules. Change in spectral response of photoconductivity and the phosphorescence efficiency when crystals are exposed to vapors suggest that surface states due to adsorbed molecules aid in recombination. Photovoltaic behavior of rectifying contacts lends credence to the hypothesis that infrared releases otherwise immobile holes.

INTRODUCTION

Electron traps play an important role in conduction processes in photoconductors, affecting such properties as spectral sensitivity of photoconductivity and time for rise or decay of photoconductivity due to intermittent irradiation (1). For highly photoconductive hexagonal cadmium sulfide, surface localization of a considerable portion of the traps has been reported (2). The extent to which these surface states modify electrical behavior of this crystal must be evaluated for proper application of photoconductivity theories based on isotropic bulk properties. Experiments are performed in which effects due to adsorbed vapors predominate in the measurements.

Since it is difficult to grow photoconductive cadmium sulfide with any degree of quantitative reproducibility of electrical and photoconductive properties, particular attention must be paid to results which indicate a consistency independent of the magnitude of observed effects. The crystals for which data are presented (3) were grown by a modified form of Frerichs' method (4). Cadmium vapor with argon as vehicular agent is fed into a spherical quartz oven to react with H_2S. Crystals grow from vapor produced by the reaction and phosphorescence observations are made on them; their red phosphorescence has been attributed to excess cadmium (5). For photoconductive measurements those crystals are chosen which show little or no red phosphorescence under ultraviolet excitation.

QUENCHING OF PHOSPHORESCENCE BY VAPORS

Red phosphorescence of these crystals is measured by means of an RCA Type 6217 photomultiplier with a red filter, such as Corning Type 2-62, covering the photosensitive surface. Crystals are placed on the filter and irradiated with a mercury vapor lamp used in conjunction with a Corning Type 7-60 ultraviolet filter. Observations are made of the photomultiplier current when vapors of iodine, hydrogen chloride, or water are introduced into the atmosphere near the crystal. A reduction in photomultiplier current is usually observed, taking place in less than one second. For a particular batch of crystals, current reduction due to iodine vapor is a factor of about 1000, the lowest measurable current being determined by ultraviolet excitation of the red filter and photomultiplier combination. With the removal of vapors from the crystal atmosphere, the photomultiplier current usually returns to its original value.

QUENCHING OF PHOTOCONDUCTIVITY BY VAPORS

Bube (6, 7), and Caspary and Müser (8) observed changes in photoconductivity of cadmium sulfide in vacuum. Caspary and Müser observed an increase of up to 20% and Bube reported an increase of more than 60%. Bube found atmospheric moisture to be responsible for decrease in sensitivity and increase in rate of current decay when the exciting light was removed.

To determine spectral photosensitivity of the crystals, they are mounted with nonrectifying indium electrodes (9) and inserted into a brass cylindrical container which can be evacuated to a pressure of about 10^{-6} mm Hg. A cylindrical heater is mounted externally. At a rate of 25°C/hr, the crystal is heated to 100°C in an atmosphere of a few microns pressure of helium to effect thermal conductivity between the brass container and the crystal, temperature being measured by a thermocouple adjacent to the crystal. The crystal is cooled to room temperature in vacuum. Measurements are made with the crystal connected in series with a direct current voltage source, of the order of 100 volts, and a current meter. Light from a 100-watt tungsten lamp is focused on the entrance slit of a Gaertner monochromator. Light from the exit slit is reflected by a concave mirror through a quartz

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[1] Manuscript received October 12, 1953. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954.

window onto the crystal in the container. The monochromator slits are kept fixed at 10μ.

Fig. 1 shows results of photosensitivity measurements for the same crystal in vacuum and after exposure to air at 45% relative humidity, room temperature. A current correction is applied so that current plotted in the figure corresponds to equal intensities at each wave length. It is seen that the effect of admitting air is depression of spectral sensitivity over the entire photoconductive spectrum, with a proportionately greater decrease in sensitivity toward the blue end. Fig. 2 illustrates measurements on another crystal. The coincidence in vacuum and in air of photoconductive response beyond the absorption edge at about 5200 Å (4) may be evidence that, for this crystal, the long wave length sensitivity is primarily determined by its bulk properties. Bube (7) varied the relative humidity and found that the effect of water vapor was current depression for wave lengths shorter than about 5,000 Å indicating that internal properties determined the long wave length response of his crystal.

Admission of iodine vapor to the evacuated container reduces current sensitivity of the crystal, with factors of 100 to 1000 being not uncommon for wave lengths shorter than 5200 Å.

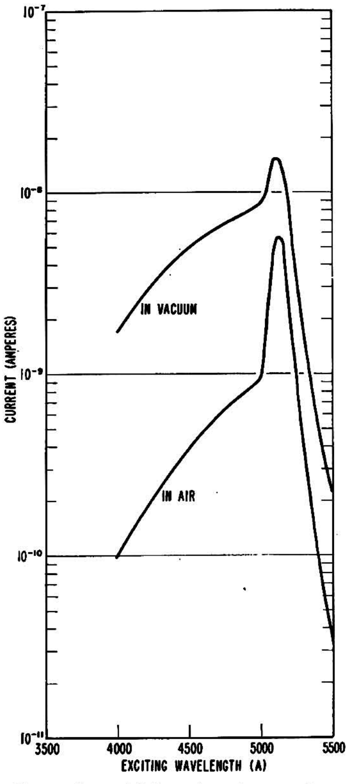

FIG. 1. Spectral sensitivity of a photoconductor before and after exposure to air.

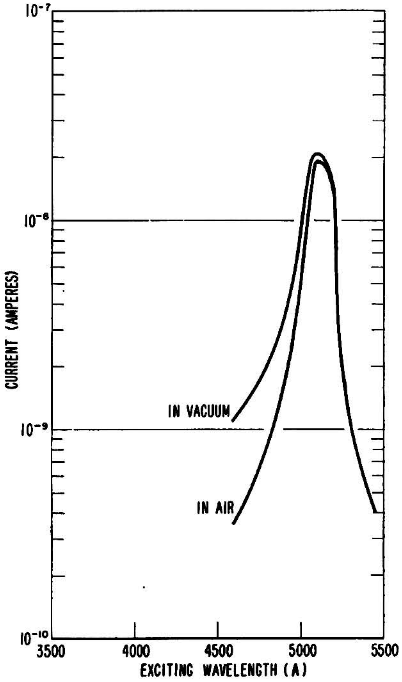

FIG. 2. Spectral sensitivity of a photoconductor with bulk effects dominating long wave length response.

RECTIFICATION

Other investigators (10–13) have reported that a potential drop usually occurred at the negative electrode on a cadmium sulfide crystal used as a photoconductor, with accompanying rectification. In repeating their experiments, it is found that rectification at broad area colloidal graphite electrodes may be enhanced by exposing the contact to hydrogen chloride for a few seconds, then washing with water. This phenomenon is apparently due to an increased capability of the crystal to take on adsorbed water vapor at the contact, since rectification is greatly diminished when the crystal is in vacuum, and is re-established when moist air is admitted. Crystals are chosen for rectification investigations by probing with a well-defined beam of light to insure that one contact is the major seat of photoconductivity.

Crystals with one predominantly rectifying contact are mounted so that two beams of light can be superimposed on the crystal. An infrared source is provided by the monochromator and lamp described earlier. The other source of light is a 100-watt tungsten lamp with a green filter. Photogenerated

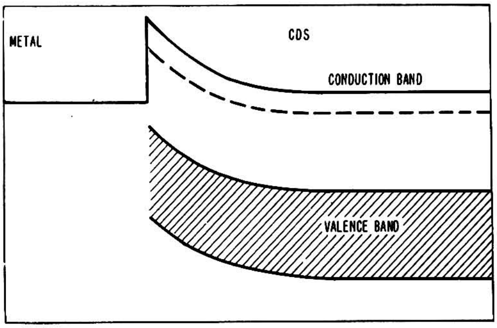

FIG. 3. Energy band diagram of rectifying contact

current at the contact is measured with a Perkin-Elmer breaker type amplifier, whose internal impedance is small compared to that of the contact, while the photogenerated voltage at the contact is measured by a Rubicon potentiometer connected so that its output voltage opposes that generated at the contact. Photogenerated voltage is given by that value of opposing voltage which nullifies current detected by the amplifier.

The effectiveness of infrared in quenching photoconductivity due to green light (2, 4, 14) is proportionately greater with the voltage applied to the crystal in the high impedance direction (electrode at rectifying contact is negative). For many crystals almost no infrared quenching is observed in the forward direction, and for some crystals there is a slight increase in current. The spectrum of infrared quenching centers at about 9000 Å and 14,000 Å identify it as the same phenomenon observed by Taft and Hebb (2).

The sign of the photogenerated voltage due to green light implies the shape of the potential barrier at the contact to be similar to that shown in Fig. 3 (15).

With green light incident at the contact, and with intensity such that photogenerated voltage is not saturated, superposed infrared light increases the generated voltage. Infrared alone produces no measurable photovoltage. Green light generates current at the contact flowing in the high impedance direction. Infrared superposed on green light increases the generated current by an amount considerably greater than is generated by infrared itself, e.g., for one crystal, infrared generated less than 10^{-11} amp, green light generated 3×10^{-11} amp, and green and infrared light combined generated 6×10^{-11} amp.

DISCUSSION

If one assumes that the effect of water vapor at the contact is similar to the effect of water vapor on the crystal surface, these observations suggest an interpretation similar to that discussed by Bardeen (16) in connection with surface states of germanium. The increase in rectification at a contact due to water vapor may be interpreted as being due to an increased number of surface states for electrons made possible by the adsorbed vapor, creating a potential barrier at the contact. The decrease in phosphorescence and photoconductivity due to vapors is explained as being due to increased recombination at the surface, a conclusion previously arrived at by Bube (7) based on photoconductivity and time constant measurements. The infrared effects at the rectifying contact may be explained by the hypothesis of Rose (1) and Taft and Hebb, (2) that infrared frees holes within the crystal. Release of positive holes in the potential barrier at the contact may heighten the barrier and increase its thickness, increasing generated voltage and current. Bube (7) attributed surface effects to a surface conductivity increased by the presence of water vapor, and implied the existence of occupied surface states on "dry" crystals due to an essential difference in the nature of the surface and volume. If the interpretation given here is valid, based on increased rectification due to water vapor at the contact and recombination enhanced by electronegative or dipolar vapors, the surface states are due to adsorbed molecules. Fig. 4 depicts the energy band diagram for a surface with adsorbed vapors.

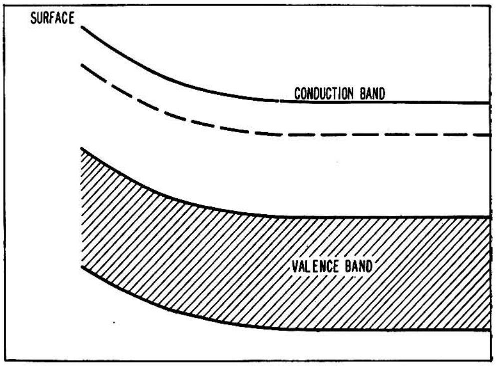

FIG. 4. Energy band diagram for surface with adsorbed vapor.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1955 issue of the JOURNAL.

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Electronic Configuration in Electrodeposition from Aqueous Solutions

I. The Effect of Ionic Structures[1]

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ABSTRACT

Consideration of electronic structures of metal ions in aqueous solutions indicates that metals are electrodeposited from ions in which coordinate linkages involve only orbitals of the outermost electronic shell. When coordination involves the penultimate shell also, that is, with Taube's "inner orbital" complexes, the metal is not electrodeposited. Apparently the energy required to break such hybridization exceeds that required for cathodic discharge of hydrogen from these solutions. Platinum metals are exceptions, probably because of extraordinary stability of the metallic state for these elements; deposition, however, requires high activation, as shown by overpotentials and low current efficiencies. Between different oxidation states, electrolytic oxidation or reduction is irreversible if the electronic configuration must be changed significantly. Irreversible deposition is observed for transition metals or when the ion is bound in a hydrolyzed aggregate. Since inner orbital hybridization is associated with a lack of substitutional lability of the coordinated groups, whereas lability of outer orbital complexes probably results from formation of a dissociation intermediate, it is likely that such an intermediate is also important in the cathode process. These considerations are used to account for and extend the Piontelli electrolytic classification of metals. In considering the effects of anions, it is shown that aquo complexes are reduced with highest irreversibility, which is attributed to high activity of water; the influence of halide ions may be labilization by the trans effect.

INTRODUCTION

Metals which have been electrodeposited from aqueous solution lie to the right of the vanadium group in the extended form of the periodic table (1). Near this boundary, deposition occurs with poor cathode efficiencies, high activation overpotentials,[3] and close dependence on conditions of electrodeposition. These circumstances suggest that the electrodeposition mechanism is seriously limited in rate, that the hydrogen discharge reaction can easily become competitive, or that both of these factors may operate. It should be noted, however, that hindered mechanisms of deposition often lead to fine-grained or even bright deposits so that deposition may be relatively simple in its technical applications.

Left of the deposition boundary line discharge of hydrogen becomes easier than that of the metal ion, while far right of the boundary, metal discharge is so easy that little or no hydrogen is produced, overpotentials are low, and ease of deposition is such that coarse, crystalline deposits are common. It is hoped, in the present discussion, to indicate reasons for these differences.

ELECTRODE POTENTIALS

Ordinarily, concentration of metal ions is sufficiently large relative to rate of deposition that concentration overpotentials do not affect the possibility of deposition. Activation overpotentials influence only rate and current efficiency. The equilibrium potential, which is decisive, expresses relative free energies of ionic and metallic states of the metal. In other words, electrode potential is determined by difference between free energy of interaction of a metal ion with whatever groups are coordinated with it in solution, and that of ion interaction with electrons of the metallic phase of the electrode.

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[3] Overpotential is used here in the ordinary sense, namely, the difference between equilibrium potential with no current flowing and the actual potential observed experimentally when metal (or hydrogen) is being deposited. For a discussion of experimental methods and interpretations, see Reference (2). When overpotentials due to ohmic resistance and concentration effects are removed either experimentally or by calculation, the remaining overpotential is regarded as due to activation requirements for the cathode process. It will be clear that overpotentials refer to kinetic effects, while equilibrium potentials refer to thermodynamic relationships.

According to Butler (3), the difference Ω in free energy between these states is measured by the sublimation energy, χ, equivalent to the lattice energy of the metallic crystals, the sum of the appropriate ionization energies, ΣI, and the coordination energy, W (which is usually simply hydration energy of the ion):[4]

$$\Omega = \frac{1}{z}(\chi + \Sigma I - W) \tag{I}$$

where z is the number of electrons involved in the electrode reaction. The applicability of equation (I) has recently been corroborated (5, 2).

For ions of alkali and alkaline earth metals, hydration energies (4) are very nearly equal to ionization energies. This has been regarded (6–8) as indicating that hydration in effect restores electrons removed in ionization. For these metals, therefore, electrode potential depends mainly on lattice or sublimation energy.

For transition metals, however, hydration energies are not as large as ionization energies; that is, coordination with water does not stabilize these ions as fully as those of alkali metals. Moreover, sublimation energies are high. Accordingly, electrode potentials are more positive than those of alkalies, so that in many cases electrodeposition of metal is favored over that of hydrogen. With zinc, sublimation energy is low, and the electrode potential is quite negative, even though the ionic state is relatively unstable. Hydrogen would be discharged preferentially were it not for its exceptionally high overvoltage on zinc.

ELECTRON CONFIGURATION AND STABILITY[5] OF COMPLEX IONS

Considering only "simple," aquated ions, energies of hydration, W, change but little through the transition series. Sublimation energies, χ, do not vary significantly. However, because ionization potentials increase, relative instabilities, ΣI-W, rise. Consequently, electrode potentials become more positive, until with chromium, metal deposition competes with hydrogen discharge. Metal deposition is increasingly favored on through the series until at copper cathode current efficiency reaches 100%.

With cyano complexes, the same trend is seen. Great stability of these complexes is expressed by high values for W. Consequently, electrode potentials are more negative than with aquo complexes, and not until copper is reached do they become sufficiently positive for metal deposition.

Thus, iron, which is deposited with some ease from hexaquo ion in sulfate baths, is not deposited from hexacyano ion. A study of a number of such series indicates that there is a shift in bond type when deposition becomes possible. In the case of iron, bonds in the cyano complex involve stable octahedral d^2sp^3 hybridized orbitals (9), while those of the aquo complex involve much less stable sp^3d^2 orbitals (10).

Since the cuprous ion has a full complement of 3*d* electrons, *d* orbitals can be made available for hybridization only by unpairing and promotion of electrons. As energy is not available for this process, only less stable orbitals are employed. Consequently, coordination energy is low, the electrode potential is more positive than that of preceding metals, and electrodeposition of copper occurs from cyano ion.

Likewise with aquo complexes, electrodeposition occurs only from ions not involving hybridized 3*d* orbitals.

Taube (10) designates such complexes as "outer orbital," while those in which *d* orbitals are hybridized with *s* and *p* orbitals of the next higher principal quantum number group are termed "inner orbital." Thus, iron is deposited readily from aquo and chloro complexes, which have outer orbital configurations, but not from cyano or *o*-phenanthrolino ions, which are of the inner type. Cadmium, which does not form inner orbital complexes because 4*d* orbitals are full, is deposited readily from cyano and *o*-phenanthrolino (11) complexes as well as from aquo and chloro ions.

From Table I it is evident that distinction between inner and outer orbital complexes is of fundamental importance in determining whether a metal can be electrodeposited from aqueous solution. Since inner orbitals represent lower energy levels than outer orbitals, inner orbital hybridization represents a configuration of greater energy of coordination, resulting in a metal complex which is more difficult to discharge than hydrogen ion (12).

According to Taube (10), a similar distinction is seen in lability of complex ions toward substitution of coordinated groups by new groups. With outer orbital complexes, substitution is ordinarily complete within a few minutes; with many inner orbital

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[4] This equation evidently suffers from two difficulties. It neglects entropy effects, which are certainly important. Furthermore, Ω is obtained as a relatively small difference between two large quantities, one of which, W, can only be determined indirectly (4) and with uncertainties which are often as large as Ω. In view of this, the agreement of Ω with electrode potentials as indicated by Piontelli (2) is surprisingly good. For purposes of this discussion, the point to be observed is the importance of coordination energy, W, in determining electrode potentials.

[5] *Stability* is used to indicate an energy relationship relative to the metallic state. Stability is often taken to refer to tendency to be transformed to the aquated or "simple" ion. As is shown shortly, such thermodynamic stability is not necessarily directly related to the stability considered here.

TABLE I. *Classification of metal complex ions according to electronic structure and character of electrodeposition from aqueous solutions.*

Inner Orbital Complexes

No deposits obtained: All complexes of Ti, Zr, Hf, V, Nb, Ta; most complexes of Cr, Mo, W; cyano complexes of Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt; *o*-phenanthrolino complexes of Fe, Co, Ni, Cu, Rh, Ir, and other platinum metals; α,α'-bipyridino complexes of Fe, Co, Ni, Rh, Ir, and other platinum metals.

Deposits obtained only as amalgams: Tetracyano nickelate.

Deposits obtained at low current efficiencies and high activation overpotentials: Many complexes of the platinum metals.

Deposits obtained at high current efficiencies and low activation overpotentials: None.

Outer Orbital Complexes

No deposits obtained: Al, Be, Mg.

Deposits obtained as amalgams only: Alkali metals, Ca, Sr, Ba; probably Sc, Y, lanthanide metals.

Deposits obtained only at low current efficiencies and high activation overpotentials: None.

Deposits obtained at high current efficiencies and low activation overpotentials: Aquo and chloro complexes of Mn, Fe (II), Co (II), Ni, Cu (II), Zn, Cd, Hg, Ga, In, Tl, Pb, Sn; pyrophosphate complexes of Cu, Zn, Cd, Sn; ammino complexes of Ni, Cu, Ag, Zn, Cd; *o*-phenanthrolino complexes of Zn and Cd; thiosulfate complexes of Cu and Ag; iodo complexes of Ag, Cd, and Hg; thiostannate; cyano complexes of Cu, Ag, Au, Zn, Cd, Hg, Tl, and In; hydroxo complexes of Zn and Sn; and others.

Notes

1. Current efficiencies are considered high, for the purposes of this table, if they exceed about 50%.
2. Activation overpotentials are considered low, for the purposes of this table, if they are markedly less than those commonly observed (2) with the transition metals and the platinum group in general, if they are less than about 0.05 volt.
3. Certain entries in the table are based on experimental work by the author to be described in a later paper.
4. Deposition from certain ions, such as Cr(III) and Co(III), although it may appear to occur from an inner orbital complex, actually takes place from a lower valence state. Details of such cases are discussed below.

complexes, substitution requires several hours. However, inner orbital complexes are labile in substitution reactions if unoccupied inner *d* orbitals remain after d^2sp^3 hybridization. Taube attributes this last type of lability to the possibility of using vacant *d* orbitals to form activated addition complexes with coordination number of seven as intermediates in the substitution process [cf. (13)]. Since reduction to metal requires removal of coordinated groups, such an addition mechanism is unlikely to facilitate deposition; accordingly, this type of substitutionally labile complex is unsuitable for electrodeposition.

In contrast, lower stability of outer orbital hybridization favors dissociation, an essential step in electrodeposition. With such complexes, Taube supposes that substitution proceeds by a dissociation mechanism. Similarly, it is likely that dissociation of one or more coordinated groups is the first step in electrodeposition.

DEPOSITION FROM LOWER COORDINATE IONS

Metals of the copper and zinc groups, which are deposited with current efficiencies of 100% under suitable conditions, have coordination numbers usually not exceeding four. For tetrahedral ions, such as zinc, cadmium, and mercuric, hybridization is outer orbital sp^3. Taube considers substitution in these ions to occur by an addition mechanism, using outer *d* orbitals. However, since metal deposition proceeds readily, it is likely that dissociation requires little energy, in accordance with the type of hybridization.

Furthermore, existence of dicyano and tricyano ions in equilibrium with tetracyano ions (14) suggests that dissociation is very easy.[6] The tricyano cuprate(I) ion is present in solutions of tetracyano cuprate (14), and copper is deposited at 100% current efficiency if the formal cyanide concentration is so limited that a substantial fraction of copper must be in tricyano form. With silver, only dicyano and tricyano complexes are known; and with gold(I), only the dicyano. As these ions are outer orbital hybrids, dissociation to a species of lower coordination number would require little energy.

Although relatively high activation overpotentials have been reported for deposition from these ions, these potentials are in reality due to concentration effects (18), for they are very highly dependent on the ratio of metal ion concentration to total cyanide concentration. Glasstone (18) found the activation overpotentials too low to be measured, and postulates such ions as $[Cu_2CN]^+$, $[Cu_3CN]^{++}$, $[Ag_2CN]^+$, and $[Ag_3CN]^{++}$ as intermediates in deposition. Evidence for such ions is found in the high solubility of silver cyanide in solutions of silver nitrate, existence of solid $2AgNO_3 \cdot AgCN$, and transport evidence for $[Ag_2I]^+$ and $[Ag_3I]^{++}$ (19). Moreover, such ions would not be repelled by negative cathode charge.

Exceptionally low thermodynamic dissociation constants of cyano complexes of copper, silver, and gold reflect high stability relative to formation of

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[6] The ions might be partially hydrated so as to retain the coordination number of four. However, the thermodynamic dissociation constant of tetracyano ion into tetraquo ion and four cyanide ions is 2×10^{-27} (15). This exceedingly low value indicates that water does not compete effectively with cyanide ion for positions in the coordination sphere. Furthermore, solid salts of the di- and tricyano ions have been obtained, with lower coordination numbers (16, 17). For these reasons, partial aquation does not seem probable.

aquo complexes, even though dissociation in the sense of loss of a cyano group with consequent lowering of coordination number evidently demands little energy. Low thermodynamic dissociation constants do not always correspond to low substitutional lability (10, 13). However, inner orbital complexes, which are so stable that the equilibrium concentration of "free" metal ion or aquo complex is experimentally inappreciable, do not undergo rapid substitutions.

According to Taube (10), the dsp^2 structure of coplanar tetracovalent ions suggests that substitution reactions will be rapid because a relatively stable p orbital is available to form an addition intermediate. This, however, would not facilitate electrodeposition, and since an inner d orbital is involved, the stability is too high to favor dissociation. Accordingly, although the tetracyano nickelate ion is particularly labile in substitution reactions, it furnishes only thin "flash" deposits in electroplating (20, 21).

However, deposition proceeds at high efficiencies and low activation overpotentials from aquo and cyano complexes of zinc and cadmium. This is to be expected from their outer orbital configurations. Platinum and palladium are deposited, though with difficulty, from square coplanar ions; yet it is clear that tetrahedral structure is far more favorable for electrodeposition than square configuration, on account of lesser stability of outer orbital hybridization.

CHANGE OF OXIDATION STATE

The ferrocyanide ion is not electrolytically reduced to metal in aqueous solutions, yet the ferrocyanide-ferricyanide couple is reversible (22). Hence activation for oxidation and reduction is low. Even though the ions have inner orbital configurations, little activation is needed for reaction (23), for no essential change in configuration occurs. Similar reversibility is observed for iron complexes of o-phenanthrolino and α,α'-bipyridine (22), which also have inner orbital structures, and others (24–33). Besides these, there are many reversible couples of outer orbital complexes for which no important change in configuration appears probable, as ferric-ferrous, thallic-thallous, ceric-cerous (34), copper complexes of ammonia and of citrate (35), and chromic-chromous (36).

But, because the ions in each pair differ in structure, change of configuration is necessary with the following irreversible couples (37): stannic-stannous, plumbate-plumbite, arsenate-arsenite (acid solution), tetracyano nickelate(II)-tricyano nickelate(I), chromate-chromic, vanadyl-vanadate, and others (38).

Evidently transfer of electrons between ion and electrode requires little activation (even where two electrons are involved, as with thallium), unless change of configuration occurs (23).

ELECTRODEPOSITION OF METALS

Chromium.—Although its hexaquo(III) ion has an inner orbital configuration, chromium is deposited from chromic sulfate baths (39). Low cathode efficiencies, often less than 50%, and high oxygen content of the deposit (1–4% as chromic oxide) indicate that reduction is difficult.

The presence of chromous ions is vital (40). Reduction to the chromous state is reversible or nearly so (36). At the dropping mercury electrode, reduction to metal proceeds through this state (41). Electrodeposition from the chromic bath is very similar to that from the chromous bath (40). It appears, therefore, that configuration of the chromous complex is decisive.

As with other complexes having four inner d orbitals occupied by single electrons, the configuration is uncertain and even the coordination number is unknown (10). Magnetic moment measurements indicate four unpaired electrons. In view of reversibility of the chromic-chromous couple (36), it may be supposed that d^2sp^3 hybridization is preserved, with the fourth electron in a $4d$ orbital. This corresponds to susceptibility of chromous ion to oxidation, but offers no explanation of deposition. It may be that the equilibrium concentration of a more favorable configuration of nearly equal energy is sufficient to facilitate electrodeposition.

Furthermore, chromic complexes show somewhat greater substitutional lability than is predicted by Taube's classification, indicating that the ion is near the arbitrary border line. This fact likewise suggests the presence of a less stable configuration.

Chromium is also deposited from the hexavalent state in chromic acid baths in presence of a critical concentration of an anion such as sulfate or fluosilicate, usually regarded as a catalyst. At best, the range of temperature and current density for deposition is sharply restricted. The cathode efficiency is generally less than 15%, and the deposit contains large amounts of hydrogen (42) and oxygen (43). Chromic ion is produced during deposition. Moreover, chromate ion is reduced to chromic both electrolytically (44) and by cathodic hydrogen (42). It has been shown that radioactive chromic ion added to the bath is not reduced to metal, suggesting that it does not participate in the electrode process (45). It is possible that access to the cathode may be denied by a barrier film (46). Both chromic and chromous states are probably involved in reduction, just as at the dropping mercury cathode (47).

Molybdenum and tungsten.—From molybdate and tungstate ions, which are of inner orbital type, the metals have been deposited as alloys with iron and other metals. The difficulty in depositing pure metals is attributed to hydrogen overvoltage effects (48). Metal deposition with cathode efficiencies of about 2% has been reported (49, 50), but deposition ceases after thin films are obtained, and the purity apparently was not examined; reduction was considered to be effected by cathodic hydrogen rather than electrolytically. Tungsten (51), but not molybdenum (52), is deposited at the dropping mercury cathode.

Cobalt.—Aquo cobalt(II) complexes are readily reduced to metal at the cathode, although with considerable activation overpotential. Reduction is also irreversible at the dropping mercury electrode. The chemical resemblance of cobalt(III) to chromium(III) complexes extends to electrodeposition (53). Cathode efficiencies are generally below 5% and many deposits are powdery. Such deposits contain considerable quantities of hydrogen and oxygen, supposedly as basic material,[7] and this indicates irreversible reduction.

Electronic configurations of cobaltic complexes, which have a special resemblance to their chromic counterparts (9), are of the inner orbital type. It is probable that deposition proceeds through the cobaltous state as at the dropping mercury electrode (54), with a change to outer orbital sp^3d^2 hybridization. Reduction of hexammino cobalt(III) ion involves aquation of the cobalt(II) ion, since the ammino cobalt(II) ion is unstable (54); pronounced irreversibility of reduction is therefore to be expected.[8]

According to Taube (10), the hexaquo cobalt(III) ion is more labile in substitution reactions than the corresponding ammino ion. Both are diamagnetic, but the paramagnetic state with sp^3d^2 hybridization is only slightly above the ground state in energy. The hexafluoro ion is paramagnetic (9, 55). As water is intermediate in polarizability between fluoride ion and ammonia, the diamagnetic state is not stabilized as much in these ions as in the ammine; Taube considers that there is a sufficient amount in the paramagnetic state to account for lability.

This circumstance would be expected to favor electroreduction of the hexaquo cobalt(III) ion, but observation of this effect would be difficult because the ion is rapidly reduced by water. In deposition from hexammino ion, cobaltous ions doubtless are reduced to metal about as rapidly as they are produced from the stable cobaltic state. Relatively high *p*H of the bath favors production of powdery deposits through partial precipitation of hydroxide or basic salts. When ethylenediamine is present these deposits are not powdery, but smooth and metallic because of stability of the chelate (53).

Nickel.—In 6-covalent nickel complexes, hybridization is either sp^3d^2, with two unpaired electrons in 3*d* orbitals, as indicated by magnetic studies, or alternatively, d^2sp^3, with the single electrons in 4*d* orbitals (10). On the basis of substitutional lability, Taube indicates that the first, or outer orbital configuration, represents hexammino and tris-(ethylenediamino) ions. From both, satisfactory electrodeposits are obtained at current efficiencies of around 90% and with high activation overpotentials.[9] The bipyridine complex is of the inner orbital type, and deposits are not obtained from it. Analogous to the ammine, the hexaquo complex is of the outer orbital type, and accounts for deposition from ordinary sulfate baths.

The cyano complex of nickel has a square, coplanar configuration, and hybridization is inner orbital dsp^2 (10). At a solid cathode, deposition is limited to a flash plate (21). As soon as the cathode is covered with nickel, the complex is reduced only to tricyano nickelate(I) ion (20). The change in configuration accounts for irreversibility of this reduction. Due to high hydrogen overvoltage of mercury, compared with that of nickel, cyano complex is reduced to the amalgam at the dropping mercury cathode, but reduction is highly irreversible (56). 4-Covalent nickel complexes are both diamagnetic and paramagnetic (57). The latter should permit electrodeposition.[10] While there is no direct evidence that paramagnetic complexes are tetrahedral, such configuration is very likely (58). The alternative explanation, that bonds are largely ionic with square configuration (59), also suggests that electrodeposition is possible.

Iron and manganese.—Iron and manganese (60) are deposited from aquo complexes with outer orbital configurations. Activation overpotentials are high. In aqueous solutions, complexes with inner orbital coordination, such as cyano compounds, are not reduced to metals. An exception is manganese, which is deposited at the dropping mercury cathode from hexacyano ion because of higher hydrogen overvoltage of mercury (61). Since iron is nearly

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[7] Considerations to be presented later suggest that this is probably water.

[8] M. W. Grieb of the University of Illinois has found that reduction is reversible in the presence of excess ethylene diamine which stabilizes cobalt(II) against aquation. The significance of this observation will be discussed in a later paper.

[9] When the current efficiency drops below 100%, the activation overpotential is high. Low overpotentials have not been observed for nickel, even when current efficiency was 100%, within experimental error.

[10] Experimental studies of electrodeposition from these complexes will be reported later.

insoluble in mercury, it is not deposited from cyano complex.

Technetium (62) and rhenium (63) have been deposited, but the character of the processes has not been reported.

Platinum metals.—In ions of platinum metals, inner orbitals are available without electron promotion, and all complexes are presumably of inner orbital type, with configurations which are either square planar dsp^2 or octahedral d^2sp^3 (64). Nevertheless, deposits of all the metals are obtained, although with low cathode efficiencies, often less than 10%.

The metals are of exceptional stability, as is evidenced by high densities and melting points. Heats of sublimation must be very high; for platinum an estimate of 4.86 ev is given (65). On this account, Ω is more positive than would be expected from stability of the complexes alone, thereby making electrodeposition possible.

In conformity with their inner orbital configurations, the octahedral complexes are not labile in substitution reactions (10). In no other instance is electrodeposition possible with substitutionally inert ions unless they pass through a labile lower oxidation state. With platinum metals, high sublimation energy appears to be decisive.

Oxidation potentials of various ion-metal couples are generally more positive than that of hydrogen by an amount sufficient to make deposition possible even if hydrogen overvoltages are ignored (66). As a direct result of inner orbital stabilities, dissociation and subsequent reductions are slow and take place at low current efficiencies and high overpotentials.

Even high sublimation energies are not enough to make deposition possible from the very stable cyano complexes, with the possible exception of those of palladium (67, 68) for which the cathode efficiency is less than 1%. However, reduction of cyano complexes to lower oxidation states is reported for all platinum metals.

Platinum is deposited from divalent chloro, nitro, ammino, phosphato, and hydroxo complexes. Deposition from platinum(IV) complexes proceeds through the divalent state. Calculations indicating high efficiencies are probably in error because of the presence of lower oxidation states (69). At the dropping mercury electrode, platinum catalyzes hydrogen evolution (70) and is not deposited under usual circumstances (68, 71).

The platinum black used in potentiometry is a typical powdery deposit. It is obtained from inner orbital hexachloroplatinate(IV) ion through the tetrachloroplatinate(II) state (72). The latter ion is also inner orbital type, like all platinum complexes, but it is thermodynamically unstable, disproportionating to give the metal and platinum (IV) ion (73), which sometimes produces colloidal metal in the bath (74), and accounts for the powdery form of the deposit. This disproportionation of an inner orbital complex reflects exceptional stability of the metallic state. However, electrolysis is apparently predominant in deposition (71).

Electrodeposition of palladium is closely similar. The tetrachloropalladate(II) ion, although somewhat more stable than the corresponding platinum complex, is rapidly reduced in the cold by hydrogen (75). It is reported that palladium is deposited at the dropping mercury electrode (68).

In electrodeposition, ruthenium, osmium, and iridium are similar to platinum. However, the actual oxidation state from which deposition occurs is uncertain, and configurations are octahedral rather than square. The metals are not deposited at the dropping mercury cathode (68).

Rhodium is deposited with comparably low current efficiencies, from trivalent complexes similar to those suitable for platinum. It is also deposited from phosphato and oxalato complexes, and from the aquo complex in sulfate, fluoborate, and perchlorate solutions with somewhat higher current efficiencies (76). Moreover, rhodium is deposited at the dropping mercury electrode (77).

Titanium and vanadium group metals.—As ions of the titanium and vanadium groups have several unoccupied *d* orbitals, their complexes are inner orbital. Consequently, deposition of the metals from aqueous solution is not to be expected. The "simple" ions are hexaquo complexes which are too stable to undergo reduction before hydrogen is discharged. Efforts to deposit the metals on solid or mercury cathodes have been unsuccessful (78).

Alkali and alkaline earth metals.—As already discussed, the negative potentials of alkali and alkaline earth metals result from low stability of the metallic state. Accordingly, the metals are not deposited except as alloys, particularly as the amalgams. In obtaining Ω, sublimation energy χ must be replaced by energy of amalgamation. This makes the electrode potential sufficiently positive to permit deposition (79). There is, of course, no possibility of inner orbital complexes; consequently deposition proceeds with very low activation overpotentials (80).

Scandium, yttrium, and the lanthanides.—Like the alkali and alkaline earth metals, lanthanides are deposited from aqueous solutions as amalgams (81), although the process is unsatisfactory on account of heavy precipitation of basic salts on mercury surface. Better results are obtained with alcohol solutions, owing partly to lower stabilities of the alcoholates. Aquo complexes have outer orbital configurations. Although yttrium is especially difficult to deposit, it is reported that scandium is reduced at the dropping mercury electrode (82). With these metals, polarographic reduction is irreversible (83) and may represent only hydrogen evolution (84). Hydrolysis accounts both for irreversibility and poor current efficiencies.

Oxidation and reduction between valences of two and three for europium and ytterbium are reversible processes (85), no change in configuration being involved.

Copper and zinc group metals.—Metals of the copper and zinc groups contrast sharply with platinum metals in depositing readily at high current efficiencies and low activation overpotentials. The contrast is somewhat less marked with iron, cobalt, and nickel. This difference is explained by filling of the *d* orbitals, so that only outer orbital complexes are formed. Furthermore, hydrogen overvoltage is high for these metals, and the complexes dissociate readily, offering little kinetic resistance to deposition.

Electrodeposition from cyano complexes has already been discussed. Because the coordination of water is weaker than that of cyanide, deposition from aquo complexes proceeds at high efficiencies and low activation overpotentials even at very high current densities.

Complexes of zinc, cadmium, and mercury(II) are tetrahedral. Deposition from the aquo, ammino, cyano, hydroxo (zincate), and pyrophosphato complexes of zinc is essentially the same process and can occur at 100% current efficiency under suitable conditions.

Metal is deposited from dicovalent aquo and ammino complexes of silver at substantially 100% current efficiencies. Similar results are obtained with complex iodides and thiosulfates.

The tetrachloroaurate(III) ion is square planar with inner orbital dsp^2 hybridization. At the cathode it is reduced to the unstable dichloroaurate(I) ion (86) which may decompose spontaneously to gold (87), although deposition appears to be largely electrolytic. The reduction to gold, therefore, occurs from an outer orbital state.

Copper is deposited at approximately 100% current efficiencies from tetraquo and tetrammino copper(II) complexes, which are square planar and therefore have been presumed to be of inner orbital dsp^2 configuration. With the ammino ion, reduction proceeds through the cuprous state (88), which is necessarily of outer orbital type. A two-stage reduction is also observed with chloro, thiocyanato, and pyridino ions. With the aquo complex, however, there is no indication of cuprous state at the dropping mercury cathode (88), yet reduction occurs with low activation overpotentials and at substantially 100% current efficiency. This is not in accord with inner orbital hybridization. Furthermore, the cupric ion forms a series of complexes containing from one to five ammino groups (89), with at least two species coexisting in considerable amounts in solution. Although equilibria indicate that the 4-coordinate ion is the most stable of the series, it does not show the exceptional stability expected for dsp^2 hybridization. Moreover, the 5-coordinate form could not have inner orbital configuration.

Magnetic moment studies (90) suggest that aquo, ammino, and certain other cupric complexes do not have inner orbital hybridization. Thus, chelate diammino complexes, which are reduced to metal in one step at the dropping mercury cathode (91), appear to have outer spd^2 hybridization.[11]

Furthermore, reversibility of the first stage of reduction of the ammino ion (88) indicates that no fundamental change in configuration occurs. Since the cuprous complex is not inner orbital, and since it is diamagnetic and has no vacant *d* orbital for hybridization, it follows that the cupric complex also is outer orbital. Thus, reversible two-electron reduction of diammines is accounted for, and since the aquo complex is similar except for weaker coordination of water, single step reduction of the aquo complex is also explained. Two steps in reduction are observed only in the presence of a coordinated group which will sufficiently stabilize the cuprous state (38).

As there is no direct evidence for the exact value of the coordination number of aquo complexes in solution, it is customary to assume that it is the same as is observed in the crystalline state. Usually this agrees with the number for the most stable ammino ion and for other typical complexes in solution (92). For inner orbital complexes, this is very probably correct, considering the special stability of this configuration. For outer orbital ions, it is required only that dissociation occur with sufficient ease to allow electrodeposition. It is, therefore, the type of bonding rather than the coordination number which is decisive.

Gallium, indium, and thallium.—The deposition of thallium (93, 94) proceeds with little activation overpotential in accordance with the outer orbital configuration. Gallium, however, is reduced irreversibly at the dropping mercury cathode (95). This irreversibility is due to binding of the ions, to greater or less degree, in colloidal sol formation by hydrolysis (96). It is therefore expected that current efficiencies at solid cathodes will be less than 100% (97).

Indium is deposited at low efficiencies from both cyanide and sulfate solutions (98). Moreover, the

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[11] An experimental study of electrodeposition from copper complexes will be reported later.

aquo complex is reduced irreversibly at the dropping mercury cathode (99). Hydrolysis (100) evidently prevents reversible reduction. In the presence of chloride ion, reduction becomes reversible at the mercury cathode (101), probably because the stable chloro complex is less readily hydrolyzed than the aquated ion. It is likely that deposition at a solid cathode will show high efficiencies from chloride baths.

Germanium, tin, and lead.—From acidified stannous sulfate baths, tin is deposited at high current efficiencies and low overpotentials which suggest reversibility. However, reduction is irreversible at the dropping mercury electrode unless chloride is present (101). The irreversibility is ascribed to hydrolysis of the aquo ion in less acid solutions, just as with gallium and indium.

Reduction of aquated stannic ion is too irreversible to be effected at the dropping mercury cathode (102). The hexachloro ion is reduced irreversibly to the tetrachloro tin(II) complex, from which reduction to the amalgam is reversible. Irreversibility of the first step is accounted for by change from octahedral to tetrahedral configuration, while reversibility of the second step is in accord with outer orbital configuration of the ion.

Tin is deposited at high efficiencies from stannite ion (103), but as this ion disproportionates spontaneously into tin and stannate (104), the deposits are usually powdery. Better deposits are obtained from the hexahydroxo stannate(IV) ion in stannate bath. Deposition proceeds through the tin(II) state, and the attendant change in configuration accounts for low cathode efficiency. The first step is irreversible, the second reversible. Stannite ions are reduced as fast as they are formed and do not accumulate in the bath sufficiently to produce a powdery deposit. At the dropping mercury electrode, reduction follows the same course through the stannous state (102).

Irreversibility of reduction from tartrate solutions (105) is probably the result of hydrolysis; irreversibility of oxidation to the stannic state is associated with change in configuration.

Lead is deposited from fluoborate, perchlorate, sulfamate, and other baths with high current efficiencies and low activation overpotentials. Reduction is reversible also at the dropping mercury cathode (106). Biplumbite ion is reduced reversibly.

Germanium is deposited from sulfate and also from germanate baths (107). Although current efficiencies were not reported, reduction is probably highly irreversible on account of hydrolysis.

Arsenic, antimony, and bismuth.—Arsenic is deposited from solutions of sodium arsenite or thioarsenite (108), but current efficiencies are not reported. At the dropping mercury electrode, arsenious acid in the presence of hydrochloric acid is reduced to the metal and arsine (109), but apparently not when other acids (110) or neutral solutions are used. Reduction is irreversible because of hydrolysis. Arsenate ion is not reduced at the dropping mercury cathode.

Antimony is deposited from a number of baths, of which the fluoride is said to be best (111). Activation overpotentials are high except in halide baths (112), because the metal is bound in hydrolysis products. "Explosive antimony" containing 10 to 15% halide (113) is produced at current densities too high for reversible deposition.

Bismuth is readily deposited (114) at very low activation overpotentials from chloride baths, but with somewhat higher polarization from sulfate solutions (115). It should be mentioned that good deposits are obtained from perchlorate baths.

Irreversible deposition from most salts of these metals suggests that oxo or hydroxo complexes are polymerized, just as with gallium (96). It has been found that bismuth exists as tetrabismuthyl ion, $(Bi_4O_4)^{4+}$, in all but highly acid solutions (55). Since arsenic and antimony are more strongly hydrolyzed, the tendency to polymerize is greater. Thus, irreversible deposition is to be expected, even though electronic configurations are outer orbital in type. The chloro complexes are more stable and hydrolyze less extensively. It has been stated that appreciable concentrations of "free" unhydrolyzed ions exist because metal can be deposited from the solutions (116). This conclusion is unjustified, for deposition probably proceeds directly from the chloro complex.

Discussion

From the foregoing, it appears that metals cannot be electrodeposited from aqueous solutions if equilibrium of the deposition reaction lies so far on the ionic side that electrode potential is more negative than hydrogen discharge potential. This occurs if: (*a*) stability of the metallic state is low, as with alkalies; or (*b*) the ionic state is especially stabilized by inner orbital hybridization (unless this is counterbalanced by exceptional stability of the metallic state).

Iron, cobalt, and nickel, although their aquo complexes are of outer orbital configuration (10), are deposited with pronounced activation overpotentials, and with lower current efficiencies than copper and zinc. Furthermore, they are reduced irreversibly at the dropping mercury cathode. In general, electrodeposition from hexaquo ions appears to be irreversible. Since 4-coordinated complexes are also well known for those metals, it might be postulated that electrodeposition proceeds through the tetraquo ion and the attendant change in configuration accounts for irreversibility. This point is to be discussed further in a future paper.

Accordingly, irreversibility of electrode reactions is explained by: (*a*) alteration of electronic configuration in change of oxidation state; (*b*) limited availability of the metal ion because it is bound in hydrolyzed polymeric aggregates; or (*c*) kinetic hindrances associated with deposition from complexes of the transition metals.

Electrolytic Classification of Metals

On the basis of behavior in electrode systems, Piontelli (6) divides metals into three classes.

Normal metals are those which: (*a*) quickly establish stable potentials when immersed in solutions of their salts, with little influence by previous treatment of the electrode metal; (*b*) are electrodeposited with low activation overpotentials, which are roughly equal at anode and cathode; (*c*) give cathode deposits with well-developed, relatively large crystals, not readily affected by addition agents in the bath (117); (*d*) are deposited with high current efficiencies, often close to 100%; (*e*) show good correlation between position in the electromotive series and behavior in displacement reactions; (*f*) are deposited reversibly at the dropping mercury cathode; and (*g*) have high hydrogen overvoltages.

Inert metals are those which: (*a*) show potentials which fluctuate widely in solutions of their salts, and are determined in part or entirely by reactions other than ionization of the metal; (*b*) are deposited with high activation overpotentials for the cathode reaction, and usually for the anode reaction as well; (*c*) are deposited as fine crystals, readily modified by action of addition agents in the bath, so that it is relatively easy to produce a "bright" deposit in technical electroplating; (*d*) are deposited with current efficiencies appreciably less than 100%; (*e*) in displacement reactions, show more nobility in the metallic state, and less in the ionic state, than is expected from their position in the electromotive series; (*f*) are deposited irreversibly at the dropping mercury cathode; and (*g*) have low hydrogen overvoltages.

Intermediate metals are those which show characteristics of both groups.

Metals with incompletely filled *d* orbitals are inert, as is to be expected since they may form inner orbital ions. Metals with filled *d* orbitals are either normal or intermediate. The behavior of copper, silver, gold, and zinc is so close to normal that they may be considered to belong to the normal class. The intermediate behavior of arsenic, antimony, and bismuth appears to be a consequence of hydrolysis of the ions.

When the behavior of amalgam electrodes is considered, alkali and alkaline earth metals are assigned to the normal class, in accordance with their electronic structures. Thus the complete classification of Table II is obtained. Normal metals come after inert gases and again after platinum metals, which have inert gas-like structures. Gallium is termed normal on the basis of stable potential of the gallium electrode. Germanium is probably intermediate due to its tendency to hydrolyze.

Effects of Anions

Electrode potentials become more negative when the concentration of coordinating species in solution increases beyond that needed to form the complex. Thus, excess (or "free") cyanide ions lower the copper potential. This shift is often incorrectly interpreted in terms of repression of dissociation of the complex into the "simple" metal ion (actually the aquo complex). The latter is often so exceedingly low in concentration that the electrode must be considered to respond to the predominant complex.

If loss of one of the coordinated groups is a controlling step in the cathode reaction, the presence of uncombined groups will shift the equilibrium toward the undissociated complex; the complex is made more stable, and the electrode potential is therefore more negative. In some instances, new complexes of higher coordination number will be formed. Moreover, there may also be a kinetic effect.

As the electrode potential becomes more negative, there is increased competition of the hydrogen discharge reaction with the deposition process. This

TABLE II. *Electrolytic classification of elements*

	H																
He	Li	Be	No deposits								No deposits		B	C	N	O	F
Ne	Na	Mg											Al	Si	P	S	Cl
A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Xe	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
Rn	Fr	Ra	Ac†														
		Normal		Inert—no deposits				Inert					Normal			Intermediate	Nonmetals

* Lanthanides. † Actinides.

TABLE III. Polarographic Half-Wave Potentials
[From Reference (94)]

Substance	Supporting electrolyte	$E_{1/2}$ vs. S.C.E volt	Difference volt
Bismuth	1*N* HNO_3	−0.01	
	1*N* HCl	−0.08	−0.07
Cadmium	1*N* KNO_2, HNO_3, or H_2SO_4	−0.586	
	1*N* KCl or HCl	−0.642	−0.056
	1*N* KI	−0.74	−0.15
Lead	1*N* KNO_2 or HNO_3	−0.405	
	1*N* KCl or HCl	−0.435	−0.035
Zinc	1*N* KNO_2	−1.012	
	1*N* KCl	−1.022	−0.010
Cobalt	None ($CoCl_2$ only)	Irreversible	
	0.1*N* KCl or NaCl	−1.20	More positive
Indium	0.1*N* $HClO_4$	−0.95	
	0.1*N* KCl or HCl	−0.561	0.39
	0.1*N* KI	−0.53	0.52
Iron (II)	1*N* NH_4ClO_4	−1.45	
	1*N* KCl or HCl	−1.3	0.15
Nickel	NH_4ClO_4 or KNO_3	Irreversible	
	1*N* KCl	−1.1	More positive
Tin	2*N* $HClO_4$	Not reduced	
	2*N* $HClO_4$ 0.5*N* NaCl	−0.35	Large positive shift

accounts for the decreased current efficiencies often observed. There may be an effect on hydrogen overvoltage also.

Furthermore, halide ions appear to facilitate deposition of almost every metal (2, 118). At the dropping mercury cathode, irreversibility of deposition of tin, cobalt, nickel, iron, and indium is either greatly lowered or eliminated by the presence of halide ions. For a number of metals, the lowest activation overpotentials, both anodic and cathodic, are observed in chloride and iodide solutions (2). Moreover, in technical electroplating, the nickel chloride bath operates at higher current densities and higher current efficiencies than the sulfate or Watts baths (119), and the character of the deposit under favorable conditions suggests that reduction is more nearly reversible.

The effect of chloride ion is attributed to formation of a chloro or chloro-aquo complex ion. Such coordinate bonds are more stable than those of the aquo ion; otherwise, of course, the chloro complex would not be formed. Increased stability raises the value of W in the expression for Ω, and the electrode potential becomes more negative.

Measurements of equilibrium potentials to test this deduction are lacking, but related polarographic half-wave potentials are given in Table III (94). The predicted negative shift is seen for bismuth, cadmium, lead, and zinc. As these are normal metals, or nearly so, activation overpotentials are small and do not mask the shift due to chloride. For the highly irreversible reductions of iron, cobalt, and nickel, large decreases in activation overpotentials evidently outweigh the effect on equilibrium potentials. With tin and indium, the shift is probably due to stabilization of the complex with respect to hydrolysis.

Activation overpotentials are generally influenced by anions. In solutions of simple salts, overpotentials usually increase in the order: iodide, chloride, sulfate, fluoborate, sulfamate, nitrate, perchlorate (2). Activation is lower with anions showing stronger tendencies to coordinate. Furthermore, when several anions are present, activation overpotential is determined largely by the anion with the strongest coordination tendency. Thus, addition of chloride ions to the solution of a metal sulfate lowers the activation overpotential to approximately that of a simple chloride solution, whereas addition of sulfate to a chloride solution has little effect. Adding cyanide ions lowers activation potentials still further, if the cyano complex is outer orbital. Similar effects of anions are observed in exchange reactions between metals and their solvated ions (120, 121).

For electrodeposition from aqueous solutions, aquo complexes generally require greater activation energies than do other types, although the former must be the least stable or else the others would not be formed in aqueous solutions. This circumstance results, of course, from the fact that overpotentials are kinetic, not equilibrium, phenomena. It may be supposed that in the dissociation step the exceedingly high activity of water in aqueous solutions affects such rapid reassociation that high activation is needed to produce sufficient quantities of the intermediate dissociated complex to allow reduction to proceed. Other complexes require less activation because the activity of uncoordinated species, such as chloride or cyanide ions, is relatively low.

It is unknown whether chloride ions form a proportion of fully chlorinated ions, or whether the aquo complexes are partly chlorinated, as $[M(H_2O)_5Cl]^-$ or $[M(H_2O)_4Cl_2]$, etc. (122). Chloro-aquo complexes are probably present in many solutions. They may require less activation for dissociation and electroreduction because of the labilizing effect of chloride ion on the aquo group in trans position according to the well-known trans effect (123). Reducibility of complex ions by molecular and atomic hydrogen is increased by this effect (124). According to Heyrovsky (125), polarization of the chloride ion facilitates electron transfer.

The deposition process may continue by discharge of the dissociated complex (71). More likely, the dissociated intermediate may be first adsorbed on the cathode surface by interaction of unsatisfied bond functions on the metal surface with orbitals of the ion vacated in dissociation. Then, with acquisition of the requisite number of electrons from the cathode, the metal ion assumes the metallic state structure and releases remaining coordinated groups (126). Effects of addition agents can then be explained by their influence on adsorption. These points will be elaborated in a later paper.

SUMMARY

In the foregoing, major characteristics of electrode systems in electrodeposition are explained on structural considerations. Inasmuch as deposition characteristics at solid and mercury cathodes are generally parallel, activation needed to build up crystal lattices of deposited metals (127) appears to be of relatively small magnitude. The sharp decrease in activation overpotential as temperature of the solution is raised suggests that the rate-controlling step is chemical, rather than electrolytic in character. Dissociation of the metal complex therefore appears to be decisive.

Hydrogen overvoltage (128) exerts a secondary influence, but it is striking that inert metals are also those with low hydrogen overvoltage. From their densities, tensile strengths, interatomic distances, melting points, etc., it is seen that inert metals form very strong bonds in both the metallic and ionic states. Accordingly hydrogen atoms should be strongly adsorbed, and equilibrium in the reaction: $M + H^+ (aq) + e^- = M \cdot H$, should lie well to the right, corresponding to low overvoltage. On the other hand, with the weaker bonds of normal metals, equilibrium lies to the left. This is in accord with conclusions of Bockris and Potter (129) that the rate determining reaction on platinum is the combination of atomic hydrogen. For silver and mercury, the relatively weak bonds to not interfere with this combination, and the discharge reaction becomes controlling. However, results with nickel are not in accord with this explanation.

Furthermore, the strength of bonds formed by inert metals in both states suggests that the potential barrier to be surmounted in passing from one state to another is high, whereas it is low for normal metals. This is in agreement with the magnitudes of activation overpotentials, and explains the rough symmetry in anodic and cathodic overpotentials (2).

Finally, standard electrode potentials for various complex ions afford estimates of relative energies of coordination through the expression for Ω. Although experimentally this can be realized only for normal metals, and should be modified by entropy changes, it provides a comparison of strengths of coordinate bonds.

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Electronic Configuration in Electrodeposition from Aqueous Solutions

II. The Deposition Process[1]

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ABSTRACT

It is proposed that electrodeposition proceeds through an intermediate complex ion adsorbed on the cathode by a coordinated bridge. Subsequently, the bridge is eliminated and a metallic bond established. By applying Pauling's theory of the metallic state, reversible deposition of post-transition metals and irreversible deposition of transition metals are explained. A close correlation with electron-transfer reactions is shown. Inclusions in deposits represent residual coordinated groups, in agreement with results of recent studies.

Introduction

Recently, reasons were given for regarding electrodeposition as closely related to the possibility of dissociation of a coordinated group from the metal ion (1). The resulting ion, which may be regarded as an activated intermediate, accordingly has a coordination number which is one less than usual. This ion may, of course, reunite with another coordination group and return to its original state. At the electrode surface, however, coordination unsaturation may be satisfied by forming a covalent bond with an electron pair of one of the surface atoms of the metal. Whether this surface compound will then be reduced to the metallic state will depend on availability of necessary electrons in the cathode metal.

Deposition of Normal Metals

Consider reduction of the normal[3] metal ion $[\mathrm{Zn(H_2O)_4}]^{++}$. Its outer electronic structure may be represented by:

$$[\mathrm{Zn(H_2O)_4}]^{++}\ \overset{3d}{\overline{:\ :\ :\ :\ :}}\ \ \overset{4s}{\overline{:}}\ \ \overset{4p}{\overline{:\ :\ :}}$$

Accordingly, the structure of the activated intermediate is:

$$[\mathrm{Zn(H_2O)_3}]^{++}\ \overset{3d}{\overline{:\ :\ :\ :\ :}}\ \ \overset{4s}{\overline{:}}\ \ \overset{4p}{\overline{\ \ :\ :}}$$

Pauling (3) considers the predominant electronic structure contributing to the resonance hybrid representing metallic zinc to be:

$$\mathrm{ZnB}\ \overset{3d}{\overline{:\ :\ :\ :\ .}}\ \ \overset{4s}{\overline{.}}\ \ \overset{4p}{\overline{.\ .\ o}}$$

where single dots represent single bonding electrons, and "*o*" indicates the so-called metallic orbital, empty except for resonating electrons. Pauling regards the metallic orbital as giving rise to special resonance which explains characteristic metallic properties. In the metal lattice, where bonding electrons are paired with electrons from neighboring atoms, the structure may be written:

$$\mathrm{ZnB}\ \overset{3d}{\overline{:\ :\ :\ :\ :}}\ \ \overset{4s}{\overline{:}}\ \ \overset{4p}{\overline{:\ :\ o}}$$

This structure is substantially identical with that of the activated intermediate, $[\mathrm{Zn(H_2O)_3}]^{++}$. In this ion, three electron pairs, $4s4p^2$, are shared with coordinated water molecules. However, in ZnB, four electron pairs, $3d4s4p^2$, are shared with adjacent zinc atoms.

Dissociation of the complex ion by loss of a coordinated group therefore amounts to opening of the metallic orbital. Loss of another coordinated group would result in two open metallic orbitals, and the ion would correspond to Pauling's ZnC configuration.

It is now proposed that opening the metallic orbital permits the intermediate complex ion to participate in metallic resonance of the cathode lattice, so that a bond which is at least partially metallic in character is established, and the ion is bound to the cathode surface. Remaining pairs of bonding electrons then have the alternatives of continuing in coordination hybridization with the remaining coordinated water molecules, or of participating in metallic resonance with neighboring metal atoms. Hybridiza-

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[3] The word "normal" is used in the sense that electrode reactions are substantially reversible, after Piontelli (2).

tion of fewer orbitals than the preferred number represents a state of less stability than that of the normal complex ion, but metallic resonance confers special stability. Consequently the latter will be preferred, if the necessary number of electrons is available to fill appropriate orbitals.

To ascertain the number of electrons required for conversion to the metallic state, it is noted that loss of the three remaining coordinated water molecules will remove all six electrons in the 4*s* and 4*p* orbitals. The ZnB structure calls for four single bonding electrons in the $3d4s4p^2$ orbitals. After loss of the water molecules, only two electrons are available, namely, those in the last 3*d* orbital. Thus, two additional electrons are needed, and if they are available in the lattice structure of the cathode, in excess of the normal quota, they will migrate to the ion, completing conversion to the metal atom.

This explanation implies that actual transfer of electrons to the ion undergoing discharge will not be much more difficult than transfer of electrons in metallic conduction. The processes are essentially similar, if not identical. This inference is in agreement with the observation that electron transfer in reduction of such ions as ferricyanide requires negligible activation (4).

The mechanism described accords more closely with the hypothesis that processes of discharge and deposition are simultaneous (5, 6) than with the view that deposition follows discharge (7). It requires interaction between ion and metal lattice as a prerequisite to neutralization of the ionic charge.

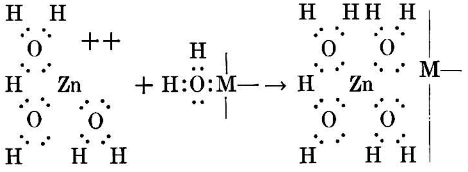
Since configurations of $[Zn(H_2O)_3]^{++}$ and ZnB are so nearly identical, it is to be expected from previous considerations (1) that the zinc electrode will be reversible[4] both anodically and cathodically. This, of course, is in agreement with facts.

Ionic and metallic structures of copper(I), silver(I), gold(I), cadmium, mercury(II), gallium, indium, and thallium(III) are essentially similar (3) to those of zinc. Ions are reduced reversibly, and presumably by similar mechanisms, except when they are bound in hydrolysis products (4).

BONDING OF METAL ION TO CATHODE SURFACE

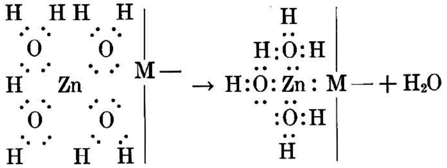
In the preceding section, it was tacitly assumed that electron pairs are available at the cathode surface for bonding with the intermediate ion, $[Zn(H_2O)_3]^{++}$. The metal surface is probably hydrated, for, in terms of the mechanism just suggested, surface atoms on deposition do not find enough adjacent metal atoms to convert all of their bonding electrons to shared electron pair bonds. Consequently, a certain number will remain in coordination hybridization with water molecules.

Therefore, it is probable that electron pairs available for bonding at the cathode surface are largely those of coordinated water molecules. It may be imagined that binding of the 3-coordinate metal ion occurs first through a water bridge:



where $\overset{|}{\underset{|}{M}}$—represents the metal atoms (in this case, zinc) in the cathode lattice structure. The activation and adsorption process is equivalent to replacement of a water molecule originally located within the coordination sphere of the undissociated ion by a water molecule which is coordinated to the metal surface; or, what is essentially the same thing, adsorption on the surface of a coordinated water molecule of the undissociated ion.

Next occurs replacement of the water bridge by a metallic resonating bond between the ion and metal atom, with simultaneous or subsequent neutralization of the ionic charge:



The process is facilitated by the geometry of the bridging water molecule which, by virtue of the angularity of its bonds, brings ion and metal atom fairly close together. The change is facilitated also by relatively great extension of 4*p* orbitals of the ion

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[4] A number of oscillographic studies (8) have shown that many electrode reactions ordinarily considered reversible are in fact irreversible. Few if any reactions are strictly reversible, just as no machines are totally frictionless. In the absence of a quantitative measure of irreversibility, the following criteria have been adopted for the present purposes:

A reaction is considered to be reversible if the activation in ordinary electrodeposition (2) amounts to no more than a few hundredths volt overpotential; or if a polarogram made under usual conditions with customary apparatus (9) gives, in plotting E vs. log $i/(i_d - i)$, a straight line with a slope within five per cent of the theoretical value (10). In this, E represents impressed voltage, i the current, and i_d the diffusion current.

Normally, reversible electrodeposition processes take place at theoretical current efficiencies, but this is not always a reliable criterion. Nickel, for example, is often deposited at theoretical efficiencies within experimental error, although it is well known to be reduced irreversibly in all cases (11).

and metal atom, so that interaction may occur more readily. Establishment of the metallic bond draws the ion still closer to the metal lattice and the bridging water molecule is expelled. It is possible that electrostatic attraction assists in this process.

Although this mechanism is purely hypothetical, it provides a plausible picture of the deposition process, which is needed to explain correlations between electronic structure and electrode behavior. Furthermore, it affords a starting point for development of the important theory of effect of surface films on electrodeposition (12). Obviously the picture is somewhat oversimplified, for it neglects effects of steric factors and of ionic double layers.

According to the proposed mechanism, small activation energies observed in electrodeposition of normal metals must consist in large part of activation required to convert coordination hybridization to metallic resonance.

The circumstance that a certain number of water molecules may remain coordinated to the metal after conversion does not affect these considerations. Partially hydrated atoms represent an intermediate stage in conversion, persisting because of the phase discontinuity at the surface. The electrode reaction is based on complete conversion to metal which is undergone by a large majority of the ions. Hence, conclusions drawn from structural similarity between the two states remain valid.

The role of the activated intermediate, $[Zn(H_2O)_3]^{++}$, is evidently in formation of the bridge-complex as a surface intermediate. Furthermore, the lability which facilitates bridge formation also facilitates expulsion of the bridge and simultaneous formation of the metallic resonating bond. Consequently, a parallelism is to be expected between readiness to undergo reactions through the activated intermediate and ease of the electrode reaction. For the sake of simplicity, electrode reactions are discussed in terms of the activated intermediate produced by dissociation of a coordinated group, although it must be understood that corresponding bridge-complexes are equally important in the proposed mechanism.

When metal ions are coordinated with groups other than water, it is supposed that one of these groups may serve as a bridge. This will be true of ammines, cyanides, halides, etc.

DEPOSITION OF TRANSITION METALS

With transition metals, which are inert according to Piontelli's classification (2, 4), the mechanism is somewhat different. First, coordination numbers are frequently six, especially for aquated ions. However, 4-coordination is also stable. In general, there is no definite indication as to the exact coordination number in solution (13).

Solutions of ammino complexes having configurations designated by Taube (14) as "outer orbital," are known to contain ions of several coordination numbers in mobile equilibrium (15). It is reasonable to assume that the situation is similar with aquo complexes. It will be assumed that deposition proceeds from tetraquo ion, which is formed as rapidly as may be needed from the other species in solution.

The activated intermediate is, therefore, the triaquo ion. For nickel and cobalt, corresponding structures are:

	3d	*4s*	*4p*
$[Ni(H_2O)_3]^{++}$	: : : . .	:	: :
NiB	: : : : :	:	: : *o*
$[Co(H_2O)_3]^{++}$	: : . . .	:	: :
CoB	: . : : :	:	: : *o*

The NiB and CoB structures are those given by Pauling (3) as contributing 65 and 70 %, respectively, to resonance hybrids representing metallic states. As before, single *bonding* electrons indicated by Pauling are shown as electron pairs to represent the states after metallic bonds are formed with adjacent atoms.

In 4*s* and 4*p* levels, configurations of ionic and metallic states are closely similar, just as in the case of zinc and other normal metals. However, for nickel and cobalt, configurations of the two states differ by two electrons in the 3*d* orbitals. Hence, transition from ionic to metallic state involves a substantial change in electronic configuration, and, therefore, according to the principle set forth previously (1), reduction must be irreversible. This prediction is in full accordance with the well-known irreversibility of nickel and cobalt electrodes.

The five 3*d* orbitals are, of course, equivalent, so that location of single electrons within the group is immaterial; only their number is significant.

Reduction may, of course, also occur from 6-coordinate ions, as well as from other complexes. Removal of electron pairs which form the fifth and sixth coordinate bonds, and are presumably located in 4*p* and 5*s* orbitals, represents an additional change in configuration. However, in view of mobile equilibria between outer orbital complex ions of different coordination numbers, this factor probably contributes little to activation and irreversibility of electrode reactions.

The mechanism proposed, therefore, starts with formation of a bridge complex at the electrode surface and subsequent elimination of the bridge, as with zinc ions. However, when metallic resonance with cathode atoms is established, electrons resonating in the 4*p* orbital may drop to vacancies in more stable

3*d* orbitals. As soon as two electrons have entered the 3*d* orbital, the resulting configuration is substantially identical with that of the metallic state. Subsequently, the state of remaining bonding electron pairs will be transformed from coordination hybridization to more stable metallic resonance, just as it was in the case of zinc. Electrons needed to neutralize the ionic charge are, of course, already present.

It may seem surprising that transfer of two electrons from the 4*p* to 3*d* level requires an appreciable activation, since stability is increased. However, the entering electrons were not originally in the 4*p* orbital, but rather in a resonance state somewhat more stable than this orbital. Apparently activation serves to lift resonating electrons to the 4*p* state momentarily, before transition to the 3*d* orbital can occur. Thus, activation represents energy needed to compensate for resonance stabilization.

This type of activation is not needed for zinc, because electrons continue to resonate in 4*p* orbitals after the ion is transformed to the metallic state, just as before transition. That is, there is no transfer from the *N* shell to the *M* shell, such as occurs with nickel.

These considerations can, of course, readily be applied to anodic processes. They can also be extended to other metals, such as iron and manganese, and to other coordinating groups, such as ammonia, chloride, or cyanide ions, as long as the complex ions do not have configurations designated "inner orbital" by Taube (14).

Platinum metals may have different electrode mechanisms, for they are deposited from inner orbital complexes. Until resonance structures contributing to the metallic state are suggested, it is difficult to propose a mechanism. Breaking of inner orbital hybridization will certainly require considerable activation. Further activation may be needed if there are other substantial differences in configuration between the two states. The highly irreversible character of electrode processes is therefore to be expected.

INCLUSIONS IN DEPOSITS

It has long been known that electrodeposits contain small amounts of oxygen and hydrogen. Frequently there are also present other substances which originate from anions or "nondepositing" cations. The presence of such impurities has often been ascribed to mechanical inclusion of adsorbed material. It is more likely that they represent coordinated groups remaining in the deposit because electron systems of a few ions were not fully converted from coordination hybridization to metallic resonating bonds.

Such incomplete conversion may occur at discontinuities in the cathode microstructure. Again, coordinated groups may not always be released if local rate of deposition becomes so high that the available time is too short for conversion of bond type and subsequent diffusion of released groups out from the cathode surface.

For every solution there is a limiting current density above which deposits become spongy (16) and contain relatively high amounts of hydrogen and oxygen. Unfortunately, no systematic study of the nature and composition of these inclusions has been reported.

It is well established that electrodeposits from chloride baths contain chlorides. It has also been claimed that sulfur is found in deposits from sulfate baths (17), but more recent studies failed to confirm this statement (18). Since chloride ion has a stronger tendency to coordinate than the sulfate, this difference is to be expected. In sulfate baths, the predominating complexes are aquated ions, and therefore it would be expected that water would be included in the deposits. In chloride baths, mixed complexes are probably present, and both water and chlorides would likely be included.

For many years it has been assumed that oxygen in nickel deposits represents basic material precipitated in the cathode film, where *p*H was presumed to be high. The precipitate was considered to be adsorbed or mechanically included in the electrodeposit (19). However, observations of the cathode film by various methods (20) fail to show the high *p*H values which would be required by this theory, although presence of a very thin film of the required *p*H is not excluded.

Recent studies (18, 21) show that the average weight ratio of oxygen to hydrogen in a large number of nickel and chromium deposits is 8.0 ± 2.6. This indicates that inclusions are water, not basic material, as predicted by the theory set forth above. Much more water is included in chromium than in nickel deposits, in accordance with comparative oxygen coordinating abilities of the two metals. Water is coordinated so firmly that it is not driven off or decomposed except at relatively high temperatures (18).

If inclusions originate from basic precipitates, deposits made at low current efficiencies will contain greater amounts of oxygen because the *p*H of cathode film will be higher. Data (18) indicate that there is no trend of this sort, although the study was not sufficiently extensive to be regarded as conclusive. Furthermore, observations of the cathode film by the drainage method (22) do not show the expected dependency of *p*H upon current efficiency. Evidence therefore indicates that inclusions are not primarily dependent upon cathode efficiency, as is required by the basic precipitate theory. However, residual coordination does not depend on either current efficiency or *p*H of the cathode film.

Nevertheless, it is possible to suggest a mechanism leading to conversion of coordinated water to basic substances which does not require an unusually high *p*H at the cathode. Upon transfer of two electrons to 3*d* orbitals of the nickel ion, a new intermediate, $[Ni(H_2O)_3]^\circ$, is produced, which has a transient existence on the cathode surface. This intermediate has an excessive number of electrons for stability. Ordinarily electrons are released along with water molecules during transition to metallic resonance. However, electrons might also be eliminated by release of hydrogen atoms from coordinated water. If two hydrogen atoms are expelled, the product would be $NiO \cdot 2H_2O$, which might be included in the deposit as hydrous nickel oxide. The net effect would be reduction of hydrogen rather than nickel from the nickel complex.

The average oxygen content observed in nickel deposits (18) indicates that this mechanism can account for only about 0.0005% of current flow, even if all the oxygen is present as $NiO \cdot 2H_2O$. Observed cathode efficiencies in nickel deposition frequently depart from the theoretical by more than 0.1% and occasionally by as much as 1–5%. At least in these cases, most of the hydrogen evolved must come ultimately from water or hydrogen ion not coordinated with nickel ion. The composition of inclusions confirms this deduction, since basic material does not seem to be prominent. Evidently activation required for metal deposition allows effective competition of the hydrogen discharge mechanism, at least in some instances.[5]

It is possible that precipitation and inclusion of basic material may become important when the bath *p*H is quite high, about 5.5 in the case of nickel sulfate. Available data (18) do not permit conclusions on this point. But at lower *p*H, inclusions from nickel sulfate baths appear to consist largely, if not entirely, of coordinated water incorporated in deposits. This observation lends support to the deposition mechanism proposed above.

COMPARISONS WITH ELECTRON TRANSFER STUDIES

Electrode processes are but a special case of electron transfer reactions, in which one reactant is a separate phase, that is, the solid or liquid electrode. Similarities between electrode reactions and electron transfer processes in general are therefore to be expected.

A summary of rates of electron transfer reactions thus far reported (23) shows that transfer is very slow whenever it necessitates a change from inner to outer orbital configuration, or vice versa. Where no shift in configuration occurs, reaction is generally complete in less than about two minutes. This is sufficiently close to the arbitrary limit of one minute selected by Taube (14) for indicating lability in substitution reactions of metal complex ions.

For example, cobalt(III) complexes are inner orbital; consequently, electron transfer from outer orbital cobalt(II) ammines is very slow (24). However, with tetraphenylporphino complex, which is very probably inner orbital in both valence states, exchange is very rapid (25). The correlation is good in a number of other instances.

From considerations based on the Franck-Condon principle (26), Libby (27) deduced a "symmetry principle," which applies to electron transfer between different valence states of the same ion in solution. It appears to be equivalent to the principle that electrolytic oxidation or reduction is reversible if no substantial change in electronic configuration is required (1). Libby predicted that the symmetry principle would be applicable at electrodes.

In iron (28), europium (29), and thallium (30) systems, it is found that electron transfer is much more rapid in the presence of chloride ions. Several investigators (4) have reported that chloride ions decrease activation overpotentials and diminish polarographic irreversibility in electrodeposition. It was previously suggested that the effect results from formation of mixed complexes such as $[Ni(Cl)(H_2O)_3]^+$. Labilization of a water group by the trans effect, according to the present theory, facilitates formation of the activated intermediate, $[Ni(Cl)\,(H_2O)_2]^+$, or more precisely, a bridge-complex in which the water bridge is labilized by the chloride ion. Concentration of the mixed complex will be proportional to the first power of chloride ion concentration. This accounts for dependence of the rate of electron transfer reaction on this quantity.

Libby considers the catalytic effect of chloride ion dependent on electrostatic forces as well as on specific complexing properties of the ions in some instances. However, it is difficult to see how such electrostatic effects can be important in the electric field at the cathode unless complexes are formed. Still, structures described by Libby resemble, to some extent, bridge-complexes in which the chloride ion functions as the bridge.[6]

[5] There is evidence that intermediates of the type described here are vital in hydrogen overvoltage phenomena.

[6] *Note added in press:* H. Taube and H. Myers [*J. Am. Chem. Soc.*, **76**, 2103 (1954)] present strong evidence for the role of an "activated bridge complex" involving chloride or sulfate bridges in electron transfer reactions. Structures proposed are strikingly similar to those here suggested for electrode reactions. Lowering of activation energy by Cl^- ions probably results, at least in part, from the formation of bridge complexes. Furthermore, the importance of bridging atoms in the electron transfer in crystalline solids has been emphasized by C. Zener [*Phys. Rev.*, **82**, 403 (1951)].

ACTIVATION STEP

Rates of exchange of cyanide ion with complex cyanides (31) show that outer orbital cyano complexes exchange rapidly, whereas inner orbital ions exchange hardly at all. This observation supports the dissociation mechanism advanced by Taube (14) to explain substitution reactions, and employed with some modifications in the present paper to account for electrode reactions. In all three classes of reactions, thermodynamic dissociation constants are misleading as to rate of reaction. This circumstance results from the difference that in rate studies, dissociation refers to actual separation of a coordinated group, while familiar dissociation constants are concerned with conversion to aquo complexes. This has been explained previously (1).

These observations, together with excellent correlation between substitution reactions and electron transfer processes, indicate that the activation process is not a result of the electric field at the cathode, nor of surface effects (8). It is therefore ascribed to thermal effects (cf. 32). This is in accord with marked reduction in activation overpotential, and consequent increase in reversibility, with rise in temperature.

ACKNOWLEDGMENTS

Valuable criticisms and suggestions have been received from Professors John C. Bailar, Jr., H. A. Laitinen, and P. E. Yankwich. The work was supported by a Pre-doctoral Fellowship awarded by the Atomic Energy Commission.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1955 issue of the JOURNAL.

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Depolarization Effects after Current Reversal at Silver Anodes and Cathodes[1]

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ABSTRACT

Anode and cathode reactions at silver electrodes in hydrogen saturated $2N$ sulfuric acid following a current reversal were studied by recording potential-time curves. Three anodic processes and three cathodic processes are indicated when the current is reversed from cathode to anode and anode to cathode, respectively. The final anode reaction is silver dissolution. Silver sulfate forms on the electrode at a critical silver ion concentration.

INTRODUCTION

Most of the work to date on electrochemical polarization phenomena has sought in one way or another to determine the nature of anode and cathode reactions. Three types of experiments have been used: (*a*) measurement of single electrode potentials at various current densities; (*b*) polarization growth and decay curves, plotting electrode potential against time; and (*c*) depolarization effects at anodes and cathodes upon current reversal. The third method is probably the most effective for electrode reaction studies and is the one used in the work described here.

The meaning of the term depolarization effect is illustrated in Fig. 1. The potential of an electrode that has been cathodically polarized is represented by the line *a–b*. At *b* the current is reversed. If the potential changes immediately to the final anodic process producing anodic polarization as along the line *bcd*, then there is no depolarization effect. If, however, there exists some kind of potential arrest, or delay in reaching the final polarization potential as *e–f* in curve *abefgd*, then there is a depolarization effect. The material producing this depolarization may be the oxidation of some material cathodically produced previous to current reversal or the formation of some anodic product prior to the final anodic process. The potentials at which depolarization effects occur are characteristic of the electrochemical reaction involved, while the coulombs of electricity consumed by the process is a measure of the amount of the material reacting at the electrode-solution interface.

Many electrode processes have been studied in recent years by means of depolarization effects at anodes and cathodes. Butler and co-workers (1–3) observed the depolarization effects of hydrogen and oxygen at bright platinum electrodes in hydrogen saturated solutions. Ferguson and Towns (4) studied anodic and cathodic depolarization curves for platinized platinum in hydrogen- and nitrogen-saturated acid solutions.

In addition to platinum, Piontelli and Poli (5) studied the cathodic depolarization processes on copper, lead, and cadmium by measuring the cathode potential at various current densities after an anodic prepolarization in acid and alkaline solutions which were saturated with air, oxygen, nitrogen, or hydrogen. In every case, a single stage of depolarization was observed and attributed to dissolved oxygen in the solution.

Luther and Pokorny (6) anodically polarized a silver electrode at a small constant current in alkaline solutions, and observed two definite arrests prior to oxygen evolution. Silver was assumed to be oxidized, quantitatively and reversibly, first to Ag_2O and then to Ag_2O_2. The cathodic reduction of the same silver oxides, formed anodically, was studied by Rollet (7). The oxidized silver electrode, with a nonpolarizing auxiliary electrode, was made the source of current which was measured as a function of time. Three level stretches of current were observed, the first was attributed to the peroxide, Ag_2O_2, the second to Ag_2O, and the last to the reduction to free silver.

The thickness of tarnish films on copper and silver were determined by Campbell and Thomas (8) from quantitative measurements on the depolarizing effects of these films while the metals were cathode in an appropriate electrolyte.

Recently, Hickling and co-workers studied the

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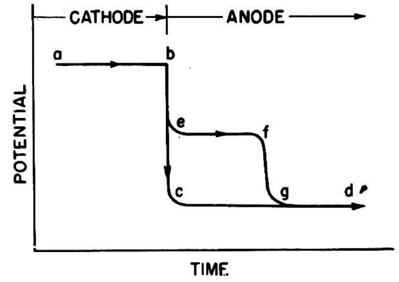

FIG. 1. Typical potential-time curves upon current reversal. (*A*) No depolarization effect, curve *a b c d*; (*B*) with depolarization effect, curve *a b e f g d*.

anodic behavior of several metals: platinum (9), gold (10), nickel (11), silver (12), and copper (13). Employing the automatic electronic system devised by Hickling (14), recurrent anode potential-time curves were obtained by means of a cathode-ray oscillograph in acid, neutral, and alkaline solutions. Breaks in the curves, in many cases, were shown to correspond to potentials of certain metal oxide electrodes prepared and measured by the authors.

In the present work, reactions at silver anodes and cathodes were studied in 2*N* sulfuric acid solutions. The experimental method employed was to record the change in the potential of a silver electrode with time following a current reversal. These potential-time curves are interpreted then in terms of specific anode and cathode reactions.

APPARATUS

The electrolytic cell used is described elsewhere (15). All potentials were measured relative to a mercury-mercurous sulfate reference electrode. Its potential against a normal hydrogen electrode at 25°C was +0.673 volt. Silver electrodes were prepared by electroplating about 0.001 in. (0.0025 cm) of silver on copper disks 1.13 cm in diameter. A cyanide silver plating solution of standard composition was used. The back side was coated with an insulating wax[3] leaving an exposed silver area of 1.00 cm^2. After plating, the electrodes were rinsed first in distilled water and then in 2*N* sulfuric acid before being placed in the cell.

Tank hydrogen was used after removing oxygen traces by bubbling through a concentrated chromous sulfate solution. The gas was then bubbled through 20% sodium hydroxide and finally through 2*N* sulfuric acid before entering the electrolytic cell.

A constant current power supply was used consisting of a 90-volt dry battery with a variable high resistance in series. Switching the current was done automatically by a specially designed photocell circuit which was synchronized to the film position of the recording drum-type camera. A block diagram of the recording and switching apparatus is shown in Fig 2. Calibration voltages and times were placed on each oscillograph record. All potential values referred to in this paper are on the hydrogen scale.

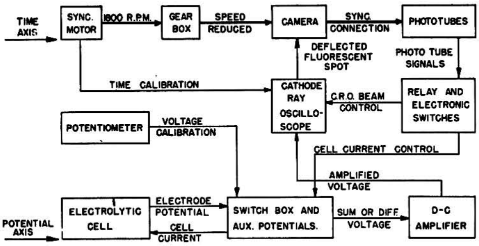

FIG. 2. Block diagram of cathode ray recording apparatus.

EXPERIMENTAL

The open-circuit potential of a silver electrode in a hydrogen saturated 2*N* sulfuric acid solution is +0.29 volt. When this electrode is made cathode at about 1.00 ma/cm^2, the electrode potential changes rapidly to that of hydrogen gas evolution. Silver ions enter the solution when the electrode is made anode. These may be removed by prolonged cathodic treatment (24 hr). The white silver surface becomes black with a finely divided, loosely adherent coating of silver. It was more convenient to use fresh solution frequently rather than electrolyze out the dissolved silver. A fresh solution was electrolyzed for about 2 hr prior to use to remove traces of metal impurities.

Anodic Depolarization Effects

In all experiments the current density, usually 1.00 ma/cm^2, was unchanged before and after current reversal. When the current is reversed making the silver electrode anode, the potential-time curve passes through several potential arrests before reaching a relatively stable anode polarization potential (Fig. 3 from *a* to *f*). After a rapid initial potential change *a–b*, a linear stage of depolarization occurs between −0.19 and +0.28 volt. This is followed by an almost horizontal potential arrest *c–d* and then a transition section *d–e*. The final anodic process begins at *e* and continues to a maximum potential of +0.70 volt. The meaning of *f* is discussed later. The amount of anodic depolarization is a function of cathodic pretreatment time. A freshly plated silver electrode usually requires several hours of cathodic pretreatment, however, before an appreciable anodic depolarization effect can be obtained. Cathodically formed anode depolarizer is always destroyed after a few minutes of anodic treatment.

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[3] United Chromium Stop-off Compound 311.

Cathodic Depolarization Effects

The typical cathodic depolarization curve obtained following an anodic pretreatment is shown in Fig. 3 from *g* to *l*. Note that there are two arrest stages of depolarization, *g–h* and *j–k*. If the current is reversed before the anode potential reaches +0.65 volt, then only one cathodic depolarization stage results, *j–k*. This indicates that the stage *g–h* is the reduction of an anodic product which begins to form at +0.65 volt. While several hours of cathodic pretreatment were required to generate an appreciable amount of anode depolarization, only a few seconds anode time before switching to cathode produced a large amount of cathodic depolarization.

Freshly plated silver electrodes were made anode at a constant current of 1.00 ma/cm^2 for various times up to 15 sec and then the current was reversed. The amount of cathodic depolarization resulting was measured on the oscillograph record from *g* to *l* (see Fig. 3). The relation between the coulombs used in the anodic pretreatment and coulombs of cathodic depolarization is given in Fig. 4. About two millicoulombs of anodic pretreatment are required to produce one millicoulomb of cathodic depolarization. Although quantitative measurements were not made on depolarization obtained with anodic pretreatments longer than 15 sec, it was observed that cathodic depolarization reached a maximum after about 1 min of anodic pretreatment at 1.00 ma/cm^2.

Electropolishing the silver electrode appeared to have no effect on anodic or cathodic depolarization curves. Freshly plated silver electrodes were electropolished in a water solution containing 100 g/l KCN and 50 g/l KOH by passing 2 amp of 60 cycle alternating current for a few seconds between the plated electrode and a coiled silver wire.

A fruitful type of experiment in this method of studying electrode reactions is to dissect polarization curves into parts (*a*) by permitting the anode or cathode prepolarization to decay briefly before current reversal, and (*b*) by reversing the current at various stages of the depolarization stage. The first type of experiment indicates what part of the initial potential change is due to a gas overvoltage since these potentials are usually large in magnitude and rapid in decay. The decay period also gives the experimenter some idea of the stability or solubility of any electrochemically formed depolarizing material in the electrolyte used. By reversing the current at various stages of the depolarization, it is possible to define clearly the individual electrode processes and determine the reversibility of each electrochemical reaction. The results of these observations are included in the discussion which follows.

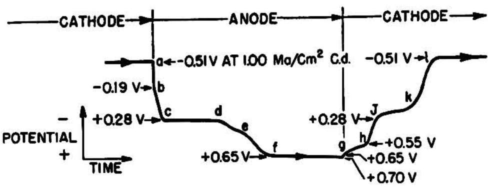

FIG. 3. Typical anodic and cathodic depolarization curves of a silver electrode in 2N sulfuric acid.

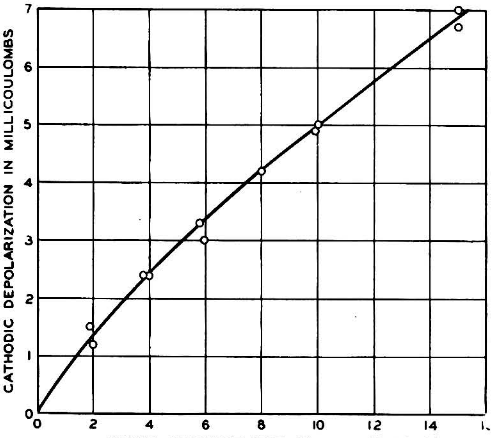

FIG. 4. Effect of anodic pretreatment on cathodic depolarization.

DISCUSSION OF RESULTS

The anode and cathode potential-time curves of silver electrodes in 2N sulfuric acid consist of several depolarization stages. Each stage corresponds to a definite electrode reaction. A symbolic description of these phases of depolarization is given in Fig. 5. Prior to *a* the silver electrode is cathode, the potential being a function of current density. At 1.00 ma/cm^2 it was −0.51 ± 0.02 volt. The electrochemical reaction occurring is

$$H^+ + e^- = H$$

The cathode potential did not change appreciably during prolonged electrolysis. A part, at least, of the cathode polarization is due to an equilibrium concentration between atomic hydrogen and hydrogen ions at the metal-solution interface.

At *a* the direction of current through the cell was reversed and the potential changed suddenly to *b*. This is the rapid portion of the cathode polarization decay which would occur regardless of whether the current was reversed or the cathode polarization simply allowed to decay on open circuit. From *b* to *c* the potential changes in a linear manner with time. This stage of depolarization is attributed to the reionization of the surface absorbed hydrogen. It can be compared to the initial anodic depolarization stage obtained with platinized platinum (4).

Beginning at *c*, the electrode passes through a region where its potential remains essentially constant. A similar arrest is observed when bright platinum electrodes are used (1–3, 16) and at approximately the same potential, +0.28 volt. Butler and Armstrong (16) explained the effect as due to the ionization of absorbed hydrogen. The actual form of hydrogen in the metal was not considered by them. Since the potential remains essentially constant in this region at both platinum and silver electrodes, it seems probable that this stage of depolarization is due to oxidation of a definite compound, in this case a hydride (17). With both metals, this stage of anodic depolarization increased with longer cathodic prepolarizations. The cathode efficiency for hydride formation appears to be very low, about 0.01% for silver. This suggests that atomic hydrogen diffuses into platinum and silver only very slowly. The stable potential of a silver electrode in a hydrogen saturated 2*N* sulfuric acid solution without any current flow was +0.29 volt. This may represent the steady condition for molecular, atomic, and ionic hydrogen at the metal-solution interface.

The amount of hydrogen available for ionization begins to decrease at *d* in Fig. 3 and the potential changes to the start of silver dissolution which begins at *e*, about +0.4 volt.

$$Ag = Ag^+ + e^-$$

The potential continues to change toward more positive values as the silver ion concentration increases. Finally at *f*, +0.65 volt, the concentration of both silver and sulfate ions exceeds the solubility product for the precipitation of silver sulfate.

$$2Ag^+ + SO_4 = Ag_2SO_4^= \text{ (solution)} = Ag_2\,SO_4 \text{ (solid)}$$

and the potential again assumes a relatively stable value due to the Ag_2SO_4 on the surface maintaining a constant concentration of Ag^+ ions. The dark, finely divided silver deposit which can be produced by plating out dissolved silver turns white soon after the electrode is made anode. This is consistent with the assumption that the compound formed is silver sulfate, since Ag_2SO_4 is white.

Experimental results indicated that no silver sulfate is produced on a silver anode in 2*N* sulfuric acid if the electrode potential does not become more positive than about +0.65 volt. Latimer (18) gives an E^0 value of +0.653 volt for the formation of silver sulfate which is precisely the value observed for the start of silver sulfate formation.

The maximum anode potential reached under all circumstances at 1.00 ma/cm² was +0.70 volt. This increase above +0.65 volt probably resulted from an excess concentration of silver ions collecting at the electrode-solution interface. In a few experiments at 1.00 ma/cm², the anode potential did not become more positive than about +0.55 volt after about 10 sec anode time. This is believed to be due to an unusual condition where atomic hydrogen was able to diffuse continuously from the metal interior to maintain the electrolysis current at the metal-solution interface, thus preventing a sufficient concentration of silver ions from building up to the point of precipitation of silver sulfate.

When the electrode polarity was reversed from anode to cathode, the material first formed anodically was reduced. The initial rapid potential rise to *g* is due to the decay of a concentration polarization produced by the slight excess of silver ions that had accumulated at the electrode surface just prior to the reversal. The cathodic depolarization stage from *g* to *h* resulted from the discharge of silver ions formed from the dissolved Ag_2SO_4 precipitate. The slope in the curve is attributed to silver ions being removed from the metal-solution interface faster than they are formed.

$$Ag_2SO_4 \text{ (solid)} = Ag_2SO_4 \text{ (solution)} = 2Ag^+ + SO_4^=$$
$$2Ag^+ + 2e^- = 2Ag$$

As all the silver sulfate is dissolved and the silver ions are discharged, the cathode potential changes

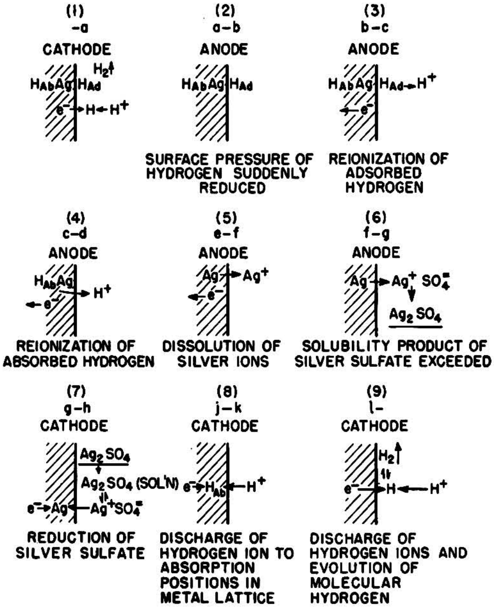

Fig. 5. Suggested reactions and conditions at the metal-solution interface at various places in the anodic and cathodic depolarization curves.

from *h* to where the next cathodic process begins at *j*. The stage of depolarization from *j* to *k* is interpreted as the discharge of hydrogen ions and subsequent absorption of the atomic hydrogen into the silver lattice, perhaps forming a silver hydride. The physical condition of the surface apparently determines how much atomic hydrogen is absorbed and thus, the length of the second cathodic depolarization stage. The length of both cathode depolarization stages is a function of the anodic pretreatment. Between *k* and *l* there is a transition from the hydrogen absorption stage to the formation and evolution of molecular hydrogen which begins at *l*. The potential at *l* corresponds to that at *a* and is a function of the current density used; at 1.00 ma/cm^2 it is -0.51 volt.

An interesting relation was observed between the coulombs used in anodically pretreating a silver electrode and the coulombs of cathodic depolarization which followed. This is shown in Fig. 4. Within the range studied, from 0 to 15 millicoulombs anode pretreatment, the total amount of cathodic depolarization observed was approximately one-half the coulombs used for the anodic pretreatment. This cannot be considered significant since some of the anodically formed silver sulfate is lost through the dissolving action of the $2N$ sulfuric acid before complete cathodic reduction of the silver ions can take place. In distilled water, silver sulfate is cathodically reduced to silver and sulfuric acid at 100% efficiency (19). While silver sulfate is essentially insoluble during the course of an experiment in distilled water, it is readily dissolved in $2N$ sulfuric acid. Results of anode polarization decay experiments show that a 10-sec anodic deposit of silver sulfate is wholly dissolved in about 5 sec decay time. The potential changes in the decay curves during the dissolving period of the silver sulfate correspond exactly to those occurring when the electrode is cathodic. This means that the potential of the electrode in the region *g–h* is controlled by the silver ion concentration at the metal-solution interface regardless of whether the silver ions are removed by cathodic electrodeposition or by diffusion and convection away from the surface. As expected, stirring shortened the cathodic depolarization stage *g–h*.

SUMMARY AND CONCLUSIONS

Three anodic processes occur at silver electrodes in $2N$ sulfuric acid when the current is reversed from cathode to anode: (*a*) ionization of adsorbed hydrogen atoms; (*b*) oxidation of absorbed hydrogen (silver hydride); and (*c*) dissolution of silver. When the silver ion concentration exceeds a critical value, silver sulfate is formed on the electrode. This film of silver sulfate is readily dissolved in the $2N$ sulfuric acid electrolyte.

Upon current reversal from anode to cathode, three cathode reactions take place: (*a*) reduction of the silver sulfate film; (*b*) discharge of hydrogen ions into absorption and adsorption positions in the silver electrode; and (*c*) discharge of hydrogen ions and formation of molecular hydrogen.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1955 issue of the JOURNAL.

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Technical Note

Continuous and Uniform Generation of Stibine

An Electrolytic Apparatus and Method[1]

Arnold Reisman[2], Melvin Berkenblit[2], E. C. Haas, and Allison Gaines, Jr.

Material Laboratory, New York Naval Shipyard, Brooklyn, New York

During the course of an investigation it was necessary to subject an instrument to an atmosphere containing a mixture of 3–4% hydrogen and $1/60$ this amount of stibine. This volume ratio had to be maintained for 24 hr. Stibine is not available commercially because it is unstable; consequently, a method was sought which would supply the gas in the desired concentration throughout the test period. A survey of available literature indicated that no reported methods would meet this requirement.

Electrolytic methods for generation of stibine using antimony electrodes have been previously reported (1, 2). These methods proved unsuitable because the production of stibine was either too low or too irregular. It was found that if the antimony electrode were replaced by a 40 gauge, platinum-iridium electrode (90:10) in conjunction with an antimony solution, stibine output at the cathode was fairly uniform and of the desired order of magnitude.

Apparatus.—The generator unit consists of a 250 ml wide-mouth Erlenmeyer flask into which is inserted an arrangement for preventing intermixing of gases liberated at the cathode with oxygen liberated at the anode. The cathode consists of a 5 mm diameter glass tube with 40 gauge platinum-iridium wire fused into one end. The anode is a 16 gauge platinum wire. A variable d-c source supplied power.

The assembly used in calibrating the generator was made up of a series of three traps followed by a conventional wet test meter, thermal conductivity bridge for measurement of hydrogen, and a regulated vacuum pump for drawing gases through the system. In order to permit uninterrupted running, two of these trap series were connected in parallel. At given time intervals the series through which the gas had been passing was removed for analysis, and the second series was brought into the circuit by means of a three-way stopcock. The first two units of each trap series contained 200 ml 0.01N iodine and 32 ml concentrated hydrochloric acid. The third unit of the series contained 300 ml 0.01N sodium thiosulfate to prevent loss of iodine by mechanical carry over.

Generating solutions.—(*A*) (4N in H_2SO_4)[3]—Dissolve 8 grams purified Sb metal in 100 ml boiling H_2SO_4, cool slightly (a white gel forms), pour with vigorous stirring into 700 ml water containing 80 grams tartaric acid, dilute to 900 ml with water.

(*B*) (1N in H_2SO_4)—Dissolve 5.3 grams Sb_2O_3 in 400 ml of solution containing 75 grams tartaric acid and 14 ml H_2SO_4, dilute to 500 ml with water.

(*C*) (0.5N in H_2SO_4)—Dissolve 7.5 grams Sb_2O_3 in 600 ml of a solution containing 77 grams tartaric and 10 ml H_2SO_4, dilute to 700 ml with water.

(*D*) (No H_2SO_4)—Dissolve 10.6 grams Sb_2O_3 in 900 ml of a solution containing 110 grams tartaric acid, dilute to 1 liter with water.

Analysis of stibine and hydrogen.—Stibine output at the cathode was determined using a modification of the iodimetric method of Haring and Compton (3). Periodically contents of the traps were mixed and back titrated with sodium thiosulfate. The quantity of stibine was then calculated using the stoichiometry given in reference (3). To determine the validity of the method, stibine triiodide resulting from the titration was converted to antimony trioxide. This was titrated with iodine to the pentavalent state (4). Results obtained from both methods checked to within 0.01 mg. Table I shows quantities of stibine as determined by the above method.

Effluent gases from the traps were drawn through a hydrogen measuring thermal conductivity bridge. Spot checks of this gas, using the conventional Orsat combustion method, were made periodically and agreed with the thermal conductivity bridge to within 0.1%.

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[1] Manuscript received August 13, 1953. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954.

[2] Present address: International Business Machines Corporation, Watson Scientific Computing Laboratory at Columbia University, New York, N. Y.

[3] Sulfuric acid was used exclusively because of its low vapor pressure. Hydrochloric acid or other acids with relatively high vapor pressure would evolve sufficient vapors to damage the instrument under test and the thermal conductivity bridge.

CONCLUSIONS

As time did not permit complete evaluation of varying conditions, a comprehensive discussion cannot be presented here. However, certain inferences can be drawn from Table I.

It was found that if any two of the three variables (acid normality, impressed amperage, and electrode length) were held constant while the third was changed, an optimum value for the variable was found to exist. Below or above this optimum value, either the hydrogen-to-stibine ratio was too great or evolution of stibine was not constant over an extended period. It is apparent, therefore, that for a given set of conditions certain combinations of the variables must be employed. These conditions, in addition to being affected by already described variables, will to a lesser extent be a function of the given stibine generator. Thus, variation in electrical components of the d-c source would require compensations and individual calibration for a given unit. The system gave the desired 60/1 ratio of hydrogen to stibine when the variables were held as shown in Table I, run 3.

TABLE I

Run No.	Generating solution	Electrode length (mm)	Amp	Time elapsed (min)	Stibine (mg/min)	Hydrogen (%)
1	I	13	1.0	60	0.24	4.4
				90	0.24	4.4
				120	0.28	4.4
				150	0.28	4.4
				180	0.27	4.4
				210	0.26	4.4
				270	0.27	4.4
				330	0.25	4.4
				390	0.26	4.4
				450	0.26	4.4
				510	0.27	4.4
				570	0.27	4.4
				630	0.25	4.4
2	I	8	1.0	30	0.50	5.3
				60	0.47	5.3
				90	0.47	5.3
				120	0.48	5.3
				150	0.41	5.3
				180	0.38	5.3
				240	0.35	5.3
				300	0.34	5.3
				360	0.32	5.3
				420	0.23	5.3
3	I	3	0.75	60	0.50	3.6
				120	0.48	3.6
				180	0.48	3.6
				240	0.49	3.6
				300	0.48	3.6
				360	0.49	3.6
				420	0.48	3.6
				480	0.50	3.6
				540	0.48	3.6
				600	0.48	3.6
				660	0.49	3.6
				720	0.48	3.6
				780	0.49	3.6
				840	0.48	3.6
4	II	10	1.0	30	0.39	4.0
				60	0.29	4.0
				90	0.25	4.0
				120	0.25	4.0
				150	0.23	4.0
				180	0.21	4.0
5	III	10	0.7	30	0.19	4.2
				60	0.07	4.2
	IV	10	0.3	30	0.08	4.4
				210	0.02	4.4

Flow was held at 0.16 l/min.

Any discussion of the paper will appear in a Discussion Section, to be published in the June 1955 issue of the JOURNAL.

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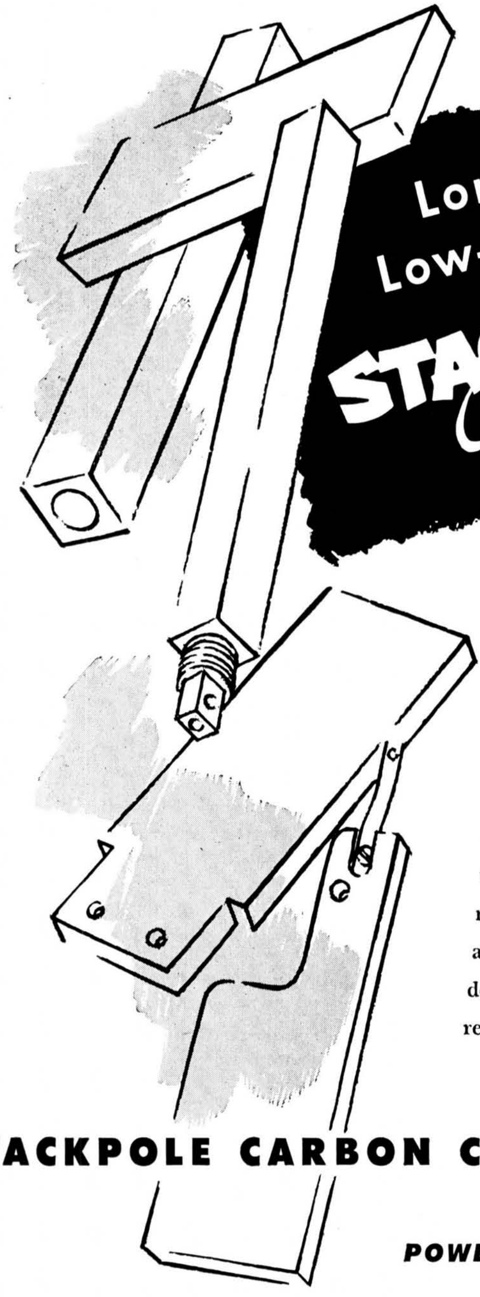

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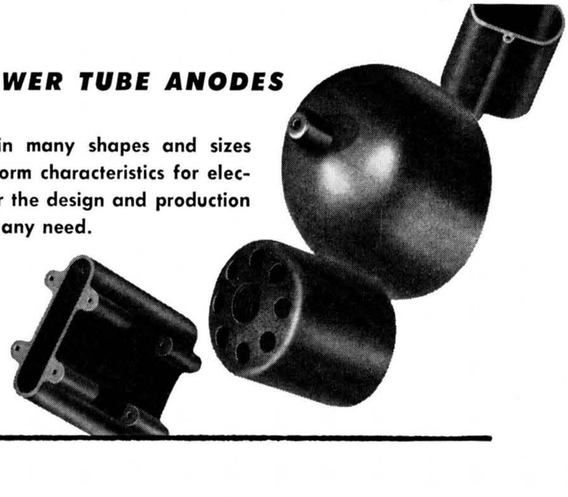

Current Affairs

Highlights of the Board of Director's Meeting

(Held May 2, 1954, La Salle Hotel, Chicago, Ill.)

Present in person were: R. J. McKay, President; M. J. Udy, President-Elect; H. Thurnauer, Vice-President; R. M. Hunter and G. W. Heise, Past Presidents; J. C. Warner, Chairman of Ways and Means Committee; R. M. Burns, Chairman of Editorial Staff; F. A. Lowenheim, Chairman of Local Section Advisory Committee; Norman Hackerman, Technical Editor; R. H. Cherry, Chairman of Electronics Division; M. L. Holt, Chairman of Electrodeposition Division; F. W. Koerker, Chairman of Industrial Electrolytic Division; R. A. Ruscetta, Chairman of Electric Insulation Division; J. P. Fugassi, Chairman of Theoretical Division; I. E. Campbell, Chairman of Electrothermic Division; E. Willihnganz, Chairman of Battery Division; H. T. Francis, General Chairman of Chicago Meeting; H. B. Linford, Secretary; and R. G. Sterns, Managing Editor.

The minutes of the previous meeting were approved as distributed.

The financial status of the Society was discussed. From all appearances, the operations this year are well within the budget. The report on the Ten-Year Index venture was made by the Secretary, showing a net profit of $2871.02 with 24 copies still on hand to be sold. This money was transferred to the Publication Reserve with the understanding that the Publication Reserve shall be used in the future to underwrite Ten-Year Indexes, insuring their continued publication.

The Secretary reported that negotiations are now under way between John Wiley and Carl Hans Verlag of Munich to arrange for German translation of "Modern Electroplating."

A communication from Dr. Uhlig was read by the Secretary in which Dr. Uhlig requested that the Board consider giving the Pacific Northwest Section a sum of $50.00 to be used for a membership campaign. The Board approved this request.

The Secretary reported on estimated costs for preparation of program booklets. The Chicago program booklet of 100 pages cost us $978.00. An estimate from Edwards Bros. for a 96-page program booklet was $550.00, provided the manuscript was sent in typed, ready for photography. It was agreed that the photo-offset method should be tried for the program booklet preparation.

The report of the Ways and Means Committee was read. This Committee recommended that the Constitution, in its current form, be presented at the annual meeting for approval. This was passed (the revised Constitution is printed elsewhere in this copy of the Journal). Bylaw changes necessitated by the change in Constitution were presented and passed.

Dr. Ivor Campbell submitted the proposition that the name of the Electrothermic Division be changed to "Electrothermics and Metallurgy Division" in conformity with the request at the Executive Committee meeting with representatives of the Rare Metals group, Electrothermic Division, and a representative of the Industrial Electrolytic Division. The official change in name was approved.

At the conclusion of the year's business, the Secretary tendered his resignation, at which time the Board voted unanimously to reappoint H. B. Linford as Secretary for the coming year. The chair was then turned over to President-Elect Marvin J. Udy, who made the following committee appointments which were all approved:

Ways and Means Committee

R. J. McKay, *Chairman*
G. W. Heise
R. M. Hunter
R. A. Schaefer
H. H. Uhlig
H. Thurnauer
F. A. Lowenheim
L. O. Case (alternate)

Membership Committee (subject to revision by the Chairman)

L. I. Gilbertson, *Chairman*
J. E. Archer
O. M. Arnold
J. R. Bukey
H. R. Copson
John Currey
H. T. Francis
J. F. Gall
A. Gunzenhauser
C. A. Hampel
A. E. Hardy
G. H. Kissin
F. W. Koerker
J. A. Lee
J. R. Musgrave
F. P. Peters
M. Sadowsky
E. A. Schumacher
D. R. Turner
R. A. Woofter
E. B. Yeager

Sustaining Membership Committee (subject to revision by the Chairman)

F. A. Lowenheim, *Chairman*
H. Bandes
G. H. Kissin
L. M. Morse
J. R. Musgrave
J. C. Schumacher

Admissions Committee

L. Weisberg, *Chairman*
Herbert Bandes
L. I. Gilbertson

Publication Committee

R. M. Burns, *Chairman*
H. B. Linford
C. V. King
N. Hackerman

Acheson Award Committee

E. G. Enck, *Chairman*
S. Swann, Jr.
J. R. Musgrave
C. C. Rose
W. Blum
H. J. Creighton
J. C. Warner
H. J. Read

Constitution & Bylaws Committee

I. E. Campbell, *Chairman* L. O. Case
F. A. Lowenheim A. C. Loonam

Finance Committee

H. Thurnauer, *Chairman* R. J. McKay
H. B. Linford E. G. Widell

Nominating Committee

G. W. Heise, *Chairman* M. L. Holt
R. M. Hunter E. Willihnganz
J. C. Warner

Patent Committee

F. W. Dodson, *Chairman*

Palladium Medal Committee

H. H. Uhlig, *Chairman*

American Association for the Advancement of Science

G. W. Heise F. A. Lowenheim

American Society for Mechanical Engineers

U. B. Thomas

American Institute of Electrical Engineers, Committee C-40

C. C. Rose

American Standards Association, Sectional Committees C-12, Z-10, Z-32, C-42

C. C. Rose

American Standards Association, Committee C-34.1

W. E. Gutzwiller

American Standards Association, Sectional Committee C-67

G. H. Fetterley

Inter-Society Corrosion Committee, NACE

H. H. Uhlig K. G. Compton

Joseph A. Holmes Safety Association

F. Ogburn

Research Council on Causes & Methods of Prevention of Internal Corrosion of Water Pipes

F. L. LaQue

The meeting was adjourned at 5:15 P.M.

Henry B. Linford, *Secretary*

Annual Report of the Board of Directors for 1953

During the year of 1953, four meetings of the Board of Directors were held. Full details of the business transacted at these meetings are contained in the minutes, on file in the Secretary's Office, where they may be consulted by any member of the Society. Only the important items of business transacted during the year of 1953 are detailed here.

During the year of 1953, your Board of Directors has been very busy preparing a revised edition of the Constitution, which it is submitting at this annual meeting for approval of members. This is a streamlined document that should improve the operating efficiency of the organization.

During the past year, the following awards were made:

Palladium Medal—N. H. Furman, Princeton University.

Young Author's Prize—W. E. Kuhn, Niagara Falls, N. Y., for his papers: "Production of Titanium Ingots by Melting Sponge Metal in Small Inert-Atmosphere Furnaces" and "Development of Graphite Electrodes and Study of Heat Losses with Different Electrodes in the Single Electrode Inert-Atmosphere Arc Furnace."

Francis Mills Turner Memorial Award, Sponsored by the Reinhold Publishing Corporation—P. T. Gilbert, London, England, for his paper: "The Nature of Zinc Corrosion Products."

Prize Essay Contest—First prize—Alvin P. Ginsberg, Brooklyn, N. Y., and Ahmad Geneidy, Morgantown, W. Va. Second prize—Robert S. Johnson, Oak Park, Ill. Honorable mention—Robert Auerbach, New York City; Herbert L. Bullard, Auburn, Ala.; Clinton Ryno, Chicago, Ill.; Elizabeth Holmes, Birmingham, Ala.; Jariwala L. Jayshri, Bombay, India; John B. Pierson, Auburn, Ala.; Richard W. Prouty, Auburn, Ala.; Roger Ray, Abingdon, Ill.; Elwood E. Richard, Oak Park, Ill.; and Warren Trask, Kirkwood, Mo.

During the past year, the Board of Directors authorized the preparation of a Ten-Year Index. This index has been published with some profit to the general funds of the Society, causing the Board to direct the national office to look forward toward continuing this Ten-Year Index indefinitely.

During the year of 1953, the national office was moved to larger, airier quarters in the same neighborhood of the city.

Your Board, at the time of the New York Meeting of the Society, took strong action condemning the dismissal of Dr. Allen V. Astin from the Bureau of Standards.

At the New York Convention, a very successful symposium on "Application of Electrochemistry to Biology and Medicine" was held. At the conclusion of this session, it was decided that a monograph based on papers presented would be of general interest to the medical profession and also theoretical electrochemists. With this in mind, Dr. Theodore Shedlovsky, of the Rockefeller Institute for Medical Research, has undertaken the preparation of this monograph.

The revised edition of "Modern Electroplating" was released by John Wiley & Sons, Inc., in November 1953. Currently, negotiations with German publishers for translation rights are being carried on.

In order that the deliberations of the Board of Directors could become more widely known to our membership, it has been decided that copies of the minutes of the Board meetings be sent to Chairmen and Secretaries of Local Sections.

Annual Report of the Secretary

Composition of Total Membership

January 1, 1954

Active	1937	
Associate	74	
Student Associate	33	
Emeritus	40	
Honorary	6	
Total		2090

Net increase during the year 1953	30
Sustaining Memberships as of April 1, 1954	80 companies
Total	119 memberships
Net increase in total Memberships	23

Report of Tellers of Election

For President: M. J. Udy, 786; 12 write-ins; 12 abstentions

For Vice-President: Norman Hackerman, 308; Fred Lowenheim, 257; J. R. Musgrave, 229; 3 write-ins; 13 abstentions

Twenty ballots were declared invalid for the following reasons: 15 ballots had more than one candidate marked for the same office, 3 ballots were completely blank, and 2 ballots contained objections to the lack of contest for the office of the President.

The ballot tabulations have been placed in a sealed envelope in the charge of Mr. Holian at The Electrochemical Society office.

(Signed) DAVID O. FEDER, *Chairman*
IRVING MOCH, JR.
WILLIAM H. REDANZ

The Tellers' Report was unanimously accepted and a motion was made declaring the candidates, M. J. Udy (President) and Norman Hackerman (Vice President), duly elected.

HENRY B. LINFORD,
Secretary

Treasurer's Report for 1953

Corrosion Handbook Fund for 1953

Total Corrosion Handbook Fund 1/1/1953		$12,399.83
Corn Exchange Bank		
USA Savings Bonds Series F (earmarked in safe deposit box)		10,471.37

CORN EXCHANGE BANK
102nd St. and Broadway, New York, N. Y.

New York Savings Bank		
Bank Balance 1/1/53		3,282.91
Credit: Interest for 1953	$ 106.64	
Royalties for 1953	1,615.40	1,722.04
		5,004.95
Debit: Prizes, Travel Expenses, Journal subscriptions, etc		555.72
Bank Balance 1/1/54		4,449.23

NEW YORK SAVINGS BANK
8th Ave. and 14th St., New York, N. Y.

Columbus Convention Fund

USA Gov't Bonds Series F (earmarked in safe deposit box)	$400.00

CORN EXCHANGE BANK
102nd St. and Broadway, New York, N. Y.

Edward Weston Fellowship Fund—for 1953

The Hanover Bank, Trustees

Capital Funds Securities, 1/1/1954

1160 Units—Hanover Bank Co., Common Trust Fund A-Value 1/1/1954—$12,299.83

$1,817.66—AC 1330 Brook Ave., Bronx, N. Y., N.Y.T. & M. Co., allowed claims

1 —Prudence 422 34 East 86th St., New York, N. Y., Mortgage Certificate

Principal Account Balance 1/1/1953	$57.31	
Credit: Payment account allowed claim 7/29/53	+19.00	
Debit: Attorneys fee on payment	−3.80	
Principal Account Balance 1/1/1954	$72.51	
Checking Account Balance 1/1/1953		$ 26.28
Credit: Deposit from Income account 9/11/1953		375.08
Checking Account Balance 1/1/1954		$401.36
Income Account Balance 1/1/1953		96.80
Credit:—Dividends from H.B., C.T. Fd. A for 1953		401.43
		$498.23
Debit: Trustees Charges for 1953	$19.74	
Transfer to Checking Acct. 9/11/53	375.08	
Income Account Balance, 1/1/1954		
The Hanover Bank Balance for Fellowship 1/1/1954		$504.77

THE HANOVER BANK, Trustees
70 Broadway, New York, N. Y.

Edward Goodrich Acheson Fund—For 1953

Capital Funds Securities—1/1/1954

$ 5,000.	USA 3¼% Treasury Bonds of 1978/83, due 6/15/83
10,000.	USA 2½% Savings Bond Series G due 11/1/54. Registered
2,000.	Pennsylvania Railroad Co. 3⅛% General Mortgage Bond, Series F. Due 1/1/85.
2,000.	American Telephone and Telegraph Co. 2¾% Debenture due 10/1/75.
52 shs.	American Can Co. 7% Cum. Pfd.
14 shs.	Corn Products Refining Co. 7% Cum. Pfd.
10 shs.	Eastman Kodak Co. 6% Cum. Pfd.
10 shs.	Ingersoll Rand Co. 6% Cum. Pfd.
25 shs.	International Harvester Co. 7% Cum. Pfd.
20 shs.	National Lead Co. Class A 7% Cum. Pfd.
1	Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Guaranteed First Mortgage Participating Certificate, Series 2-7165 Bond & Mortgage. Only remaining asset is General Claim.
1	Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Series 3-6902 due 3/1/38. 5½%
1	Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Guaranteed First Mortgage Certificate in Bond & Mortgage of Chatsworth Gardens Corp. Series 6-6972 Certificate #296. Only remaining asset is General Claim against former guarantor.

GUARANTY TRUST COMPANY OF NEW YORK
Custodian.

Fifth Ave. at 44th St., New York 18, New York.

Acheson Fund Total Balance 1/1/1953		$1,484.12
Guaranty Trust Co., *Custodian*		
Income Balance, 1/1/1953 (includes Prin. Fds. of $97.43)		747.62
Credit: Dividends plus interest on stock and bonds		1,092.84
		1,840.46
Debit: Custodian charges	$74.50	
Adjustment of Interest on Treas. Bonds	52.88	127.38
Income Balance 1/1/1954 (incl. Prin. Fds. of $97.43)		1,713.08
East River Savings Bank, Amsterdam Ave. at 96th St., New York, N. Y.		
Principal Funds Balance, 1/1/1953		736.50
Credit: Interest for 1953		18.51
Principal Funds Balance 1/1/1954		755.01
Acheson Fund Total Balance 1/1/1954		$2,468.09

Consolidated Fellowship Fund—For 1953

National City Bank, 111th St. & Broadway, New York, N. Y.		
Bank Balance 12/31/52		$14,123.37
Credit: Cash dividends from Funds		128.94
		$14,252.31
Debit: 314 shares of Wellington Fund	$7,138.60	
314 shares of Fundamental Investors	7,080.39	
Banking services	11.37	14,230.36
Bank Balance 12/31/53		$ 21.95
Capital Funds Securities		
Wellington Fund, Inc.		
The Corporation Trust Co., Agent		
120 Broadway, New York 5, N. Y.		
Shares Purchased		314.000
Shares credited in dividends, 1953		17.156
Total shares 12/31/53		331.156
Net Asset Values, 12/31/53 at $20.12/share		6,662.87
Fundamental Investors, Inc.		
City Bank Farmers Trust Company, Agent		
22 William St., New York 15, N. Y.		
Shares Purchased		314.000
Shares Credited on dividends, 1953		12.429
Total Shares 12/31/53		326.429
Net Asset Values, 12/31/53 at $19.02/share		6,208.68
Total Value of Fund Securities, 12/31/53		$12,871.55

Joseph W. Richards Memorial Fund

Bank Balance 1/1/53	$731.00
Credit: Interest for 1953	18.41
Bank Balance 1/1/54	$749.41

CENTRAL SAVINGS BANK
Broadway at 73rd St., New York, N. Y.

* * *

Summary of Changes in Constitution

Below is a summary of the major changes made in the Constitution. The proposed Constitution is printed on p. 178*C* of this JOURNAL.

ARTICLE I, Section 2, has been reworded to be in exact conformity with the purposes as stated in the Articles of Incorporation.

ARTICLE II. The first eight sections are practically identical with the former Constitution. Slight changes in wording have been made to clarify and condense the content. Section 9 has been added. This addition is as follows:

> "Section 9. Any active member who has paid dues for thirty-five years and has retired from active scientific work may ask for Emeritus membership. Emeritus members shall pay such dues and registration fees at National Conventions as are set forth in the Bylaws."

ARTICLE III in the revised Constitution covers the material previously contained in Articles III and IV of the old Constitution. The principal change here is the mechanism by which elections to membership are conducted. Under the proposed Constitution, the Admissions Committee makes recommendations to the Board. Each month the Secretary submits the list of members recommended by the Admissions Committee for a mail vote of the Board of Directors. This will speed up admission procedure.

ARTICLE IV of the revised Constitution is practically the same as Article V of the old Constitution with slight rewordings only.

ARTICLE V in the revised Constitution covers the material formerly contained in Article VI. In this revised edition, the timing of the nominations has been changed so that the Nominating Committee will be appointed at the spring meeting of the Society, making it possible to have members from various sections of the country on the Nominating Committee. The Committee will meet during the course of the spring meeting of the Society. Since its report must be made by June 15, this gives sufficient time for publication of the Nominating Committee's recommendations in the JOURNAL before balloting is required. The provision that the Treasurer may be re-elected once has been eliminated, making it possible to re-elect the Treasurer as many times as is desirable.

ARTICLE VI, Section 1, changes the composition of the Board of Directors. In the past, the Secretary has been a member of the Board of Directors, but this was changed in intent at the time the job turned into an appointive, rather than an elective, position. This now officially leaves the Secretary off the Board. Furthermore, the Chairman of the Local Section Advisory Committee is dropped, due to the fact that the local sections are setting up, by this Constitution, a new mode of operation in which a Council of Local Sections will be formed. The Council then elects two members of the Board of Directors. This will be described in more detail in Article VII of the revised Constitution. The remainder of this article is essentially unchanged.

ARTICLE VII in the revised Constitution gives constitutional status to divisions and local sections, and at the same time authorizes the local sections to organize a Council of Local Sections.

ARTICLE VIII is unchanged.

ARTICLE IX is unchanged.

ARTICLE X is unchanged.

The Revised Constitution Needs Your Approval

At the annual meeting of the Society held in Chicago, Illinois, May 2, 1954, a revised Constitution was presented. This Constitution is printed below and, according to Article X, "Final approval shall proceed through mail vote of membership, requiring a majority."

A postcard, to be used for these amendments, will be mailed to all active members early in July. Your cooperation is requested in getting this vote recorded in the headquarters office.

Constitution of The Electrochemical Society, Inc.

Article I

NAME AND OBJECT

Section 1. The name of this organization shall be The Electrochemical Society, Inc.

Section 2. The purpose for which it is to be formed is the advancement of the theory and practice of electrochemistry, electrometallurgy, electrothermics, and allied subjects. Among the means to this end shall be the holding of meetings for the reading and discussion of professional and scientific papers on these subjects, the publication of such papers, discussions, and communications as may seem expedient, and cooperation with chemical, electrical, and other scientific and technical societies.

Article II

MEMBERSHIP

Section 1. The membership shall consist of active, student associate, associate, sustaining, honorary, and emeritus members.

Section 2. An active member shall: be interested in electrochemistry or allied subjects; be at least 25 years of age; and possess a Bachelor's or Engineering degree with a major interest in the natural sciences, and have three or more years of postgraduate experience. The degree of Master of Science (or of Engineering) shall be equivalent to one year of experience and the Doctor's degree in Science (or in Engineering) shall be equivalent to three years' experience. In lieu of a scholastic degree, ten years of experience in electrochemistry or allied subjects shall be required. One year of college work in natural science shall be deemed the equivalent of one year of experience. Election to active membership shall require, in addition, recommendation by two active members of three years' or longer standing in the Society.

Section 3. A student associate member shall be at least 18 years old and shall be a bona fide student in a Natural Science or Engineering course and shall be under 29 years of age. Election to student associate membership shall require recommendation by at least two active members of three years' or longer standing in the Society. No student membership shall extend beyond the year in which the members becomes 28 years of age.

Section 4. An associate member shall have received a Bachelor's or Engineering degree, with majors in Natural Science, but not yet have completed the requirements of three years' experience nor have exceeded the age of 28. Election to associate membership shall require recommendation by at least two active members of three years' or longer standing in the Society. No associate membership shall extend beyond the year its holder becomes 28 years of age.

Section 5. Exceptions to satisfy the specifications in Sections 3 and 4 will arise when individuals have entered college or the electrochemical profession later than usual. The Board of Directors shall be empowered to waive the requirements of Sections 3 and 4, providing, however, that they preserve the intent of these sections.

Section 6. All members in good standing, elected prior to January 1, 1950, became "active" members on that date.

Section 7. Sustaining members shall be those who, through their interest in electrochemistry, contribute financially to the support and development of the Society.

Section 8. Honorary members shall be those individuals who, by reason of valuable contributions to electrochemistry, deserve special recognition by the Society.

Section 9. Any active member who has paid dues for thirty-five years and has retired from active scientific work may ask for Emeritus membership. Emeritus members shall pay such dues and registration fees at National Conventions as are set forth in the Bylaws.

Article III

ADMISSION AND DISMISSAL OF MEMBERS

Section 1. Those who prior to April 6, 1902 complied with the membership regulations then in effect are Charter Members of the Society.

Section 2. Application for membership as a student associate, associate, or active member shall be in writing on a form adopted by the Board of Directors to conform with the qualifications for membership as set forth in Article II.

Section 3. A Committee of three active members is hereby set up, to be called the "Admissions Committee," which shall receive from the Secretary all properly executed and properly recommended applications for admission which he has received from persons desirous of becoming members of this Society. The Admissions Committee shall be appointed annually by the Board of Directors, and it shall be the duty of this Committee, after examining the credentials of applicants, to make appropriate recommendation to the Board as to the fitness of all applicants for membership in this Society. Unanimous approval of an applicant by this Committee shall be required before the candidate's name can be submitted to the Board of Directors for election. The election to membership shall be by a mail vote of the Board of Directors. The candidate shall be considered elected two weeks after the date the proposed membership list is mailed to the Board, if no negative votes have been received by the Secretary's Office. If a candidate receives one negative vote his application shall then be considered and voted upon at a duly called meeting of the Board of Directors. Two negative votes cast at this meeting shall exclude a candidate. The Board of Directors may refuse to elect a candidate who, in its opinion, is not qualified for membership. The names of those elected shall be announced to the Society. A candidate who has been duly elected shall be placed on the rolls and have all the rights and privileges of a member as soon as his entrance fee and dues for the current year have been paid.

Section 4. A member desiring to resign shall send a written communication to the Secretary, who shall report it to the Board of Directors who shall accept and announce the resignation provided the dues and other indebtedness of that member have been paid up to the time of mailing of his resignation.

Section 5. Upon the written request of ten or more active members that, for cause stated therein, a member be dismissed, the Board of Directors shall consider the matter and, if there appears to be sufficient reason, shall advise the accused of the charges against him. He shall then have the right to present a written defense, and to appear in person before a meeting of the Board of Directors, of which meeting he shall receive notice at least twenty days in advance. Not less than two months after such meeting, the Board of Directors shall finally consider the case and, if in the opinion of the majority of the Board of Directors a satisfactory defense has not been made, and the accused member has not in the meantime tendered his resignation, he shall be dismissed from the Society.

Section 6. Sustaining members shall be admitted upon the approval of the Board of Directors.

Section 7. Honorary members shall be recommended over the signatures of at least ten members, and shall be elected only at the meeting of the Board of Directors in conjunction with a general meeting of the Society, and by the unanimous vote of the Directors, a quorum being present.

Honorary members shall pay no entrance fee or annual dues, and shall receive the Journal of the Society free of charge.

The number of honorary members shall not at any time exceed ten, and not more than two shall be elected in any one calendar year.

Section 8. The entrance fee, annual dues, and any other payments to be made by members of the Society shall be paid in accordance with regulations set forth in the Bylaws.

Section 9. Any member delinquent in dues after April 1 of each year shall no longer receive the Society's publications and will not be allowed to vote in any Society election until such dues are paid. All members in arrears for one year after the first of April shall lose their membership status and can be reinstated only by action of the Board of Directors.

Article IV

OFFICERS

Section 1. Only active members are eligible to hold office in the Society. The Officers of the Society shall be a President, three Vice-Presidents, a Secretary, and a Treasurer, who shall hold office as follows:

Section 2. The President, for one year. All other officers, except the Secretary, for three years. Each year a President and one Vice-President shall be elected. At triennial periods beginning with the annual meeting of 1949 a Treasurer shall be elected. The terms of office of the several officers shall begin at 8:00 A.M. of the last day of the spring meeting or convention, prior to which they shall have been elected, and each officer shall hold office until his successor has qualified.

Section 3. A vacancy in the office of President shall be filled by the senior Vice-President. All other vacancies shall be filled by the Board of Directors.

Section 4. No elective officer shall receive, directly or indirectly, any salary, compensation, or emolument from the Society, either as such officer or in any other capacity, or be financially interested, directly or indirectly, in any contract relative to the operations conducted by the Society or in any contract for furnishing supplies thereto, unless authorized either by the Bylaws or by a vote of the majority of the entire Board of Directors.

Section 5. No revision or amendment of this Constitution shall affect the tenure of office of any duly elected and incumbent officer.

Section 6. After 8:00 A.M. of the last day of the spring meeting or convention of 1952, the Secretary shall be appointed by the Board of Directors and shall serve under conditions set by, and at the pleasure of, the Board of Directors.

Article V

ELECTION OF OFFICERS

Section 1. At the organizational meeting of the Board held at the spring meeting or convention in which the new officers take office, the Board of Directors shall appoint a Nominating Committee of five members, not more than two of whom may be officers or directors of the Society. The Nominating Committee shall send to the Secretary, prior to June 15, its nominations for one or more candidates for each of the offices to be filled, except that for the Vice-Presidency at least two persons shall be nominated.

It shall be the duty of the Nominating Committee to notify each candidate of his selection and any candidate desiring to do so may withdraw his name within one week of such notification.

Section 2. The Secretary shall present the report of the Nominating Committee to the Board of Directors between June 15 and July 15, either at a meeting or by mail.

Section 3. At a Directors' meeting held prior to November 15 each year, the Board of Directors shall appoint three tellers, who shall not be members of the Board of Directors, and three alternates. Should the Directors' meetings not be held, the President shall appoint these tellers, who shall be notified by the Secretary.

Section 4. The Secretary shall mail to every active member, on or before September 15, a ballot containing the names of all candidates thus nominated. An active member's vote for officers shall not be restricted to the Nominees whose names appear on the ballot. Only active members are eligible to vote, and voting shall be by secret letter ballot; the voter shall sign his name on an outside envelope, and the ballots shall be enclosed in an inner sealed and unmarked envelope.

Voting envelopes must reach the Secretary before the fifteenth day of December.

Section 5. No person may become a candidate for the Presidency or Vice-Presidency of this Society, who has not been a member of the Board of Directors; or who has not rendered some signal service to the Society, or who is not active in the affairs of the Society. This Section of the Constitution must be printed on the ballots prescribed by Section 4 of this Article.

Section 6. The tellers shall meet for secret tallying of ballots as soon after the fifteenth day of December as possible. The Secretary shall deliver to the tellers all ballots received prior to December 15, eliminating all ballot envelopes received from members not entitled to vote because of nonpayment of dues.

All ballots shall be returned to the Secretary, who shall preserve them for one month. At the end of one month the Secretary shall return to the senders all rejected envelopes and shall open all unidentified envelopes. The eligible candidate receiving the greatest number of votes for an office shall be considered elected. The tellers shall prepare and sign a report of the results of the election, which shall be handed, sealed, to the Secretary, who shall forward it to the President, before the first day of January, who in turn shall notify all candidates of the results of the election. The results of the election shall be published as soon as possible thereafter in the Society's JOURNAL.

Section 7. At the request of the Board of Directors, the tellers shall count the ballots of any mail vote of the Society.

Section 8. The President and Vice-Presidents shall, after the expiration of the full term of office to which they were elected, be ineligible for immediate reelection to the same office.

Article VI

MANAGEMENT

Section 1. The affairs of the Society shall be managed by a Board of Directors under this Constitution and Bylaws. The Board of Directors shall be composed of the President, the immediate Past President, the three (3) Vice-Presidents, the Treasurer, the Chairman of the Publication Committee, the Chairman of the Membership Committee, two directors to be elected by the Council of Local Sections as provided in Article VII herein, and the Chairmen of the several Divisions of the Society. The President, Vice-Presidents, and Treasurer of the Society shall hold the same offices in this Board of Directors. Eight Board members, or their proxies, shall constitute a quorum.

Section 2. The Board of Directors shall prepare and adopt a series of Bylaws which shall govern its meetings and its procedure, as also that of the Society, under this Constitution. It shall require a two-thirds vote of the whole Board to adopt or amend these Bylaws; proxy and mail votes shall be counted when received before the vote is counted. The text of the proposed Bylaws or amendments shall be furnished to each member of the Board of Director at least ten days before the meeting at which the vote on the same is to be taken.

Section 3. The Board of Directors may delegate any or all of its powers, except in those cases in which the Constitution requires a vote of the whole Board, to an Executive Committee of not less than five members of the Board of Directors. The President and the Treasurer shall be members of this Executive Committee. This Committee shall conduct the affairs of the Board of Directors between its meetings. All members of the Board of Directors shall receive notice of the meetings of this Executive Committee and shall have the right to attend and vote. A majority of the Executive Committee shall constitute a quorum.

Section 5. The duties of the President, Vice-Presidents, and Treasurer shall be such as usually pertain to the offices they hold, besides any other designated in the Constitution or Bylaws or by the Board of Directors. The Secretary shall be in administrative charge to direct and supervise the duties usually pertaining to this office or designated in the Constitution or Bylaws or by the Board of Directors. The Secretary shall in all matters concerning the affairs of the Society carry out the prescriptions of the Constitution, Bylaws, rulings, and precedents, and in cases in which no such prescriptions exist, he shall obtain decisions from the Board of Directors or Executive Committee or, if time does not permit, he shall confer with the President. All funds expended in the Secretarial duties shall be under the control of the Secretary, who shall be responsible to the Board of Directors for proper expenditure of such funds. The Secretary and the Treasurer shall present reports to the Board of Directors before the annual meeting. The Board of Directors shall present a report to the Society at the annual meeting. The nature of these reports shall be specified in the Bylaws.

Section 6. All standing committees shall be directly responsible to the Board of Directors, and shall be appointed by the President subject to the approval of the Board of Directors.

Section 7. Any member of the Board of Directors, who finds that he is unable to attend a regularly called meeting of the Board, shall have the privilege of appointing a proxy to act in his stead at such meeting. The person appointed to act as proxy shall be an active member in good standing in the Society and, if appointed by a chairman of a division or of a committee, shall preferably be a person conversant with the work of that division or committee. No member of the Board shall have the power to grant to any person a proxy for more than one meeting.

Article VII

DIVISIONS AND LOCAL SECTIONS

Section 1. Professional groups representative of the several branches of electrochemistry, to be known as Divisions of the Society and to be organized from its members, may be authorized by the Board of Directors.

Section 2. A Division shall have the right to make rules for its own government, subject to the approval of the Board of Directors, not inconsistent with the Constitution and Bylaws of the Society.

Section 3. The Divisions shall be represented on the Board of Directors by their several Chairmen as provided in Article VI.

Section 4. Members of the Society residing in a given locality may organize themselves into Local Sections, subject to the approval of the Board of Directors. Not more than one Local Section may be organized in a given locality.

Section 5. A Local Section shall have the right to make rules for its own government, subject to the approval of the Board of Directors, not inconsistent with the Constitution and Bylaws of the Society.

Section 6. The several Local Sections shall be organized into a Council of Local Sections. Each Local Section shall be entitled to representation upon the Council. The Council shall make rules for its own government, subject to the approval of the Board of Directors and of the Local Sections represented and not inconsistent with the Constitution and Bylaws of the Society. The Council of Local Sections shall be entitled to representation on the Board of Directors as provided in Article VI.

Article VIII

MEETINGS

Section 1. The annual business meeting shall be held between April 1 and July 1, at such time and place as the Board of Directors shall designate. Business affecting the organization of the Society shall be transacted only at the annual meetings. Proxy or mail votes shall be honored.

Section 2. Other meetings may be held at such times and places as the Board of Directors shall select. The President shall call a meeting at the written request of thirty or more active members.

Section 3. Notice of all ordinary meetings shall be sent to all members at least twenty days in advance, and of the annual meeting, thirty days in advance.

Section 4. Any ten active members at a meeting of the Society may require that any motion brought up be submitted to a referendum of the Society by a mail vote.

Article IX

GENERAL

Section 1. A quorum of the Society shall consist of fifty active members, present in person or by proxy.

Section 2. Only those active members whose dues have been paid for the current fiscal year shall be entitled to vote at any meetings. A member may vote by proxy or by mail. No proxy shall be valid after the expiration of eleven months from the date of its execution. Every proxy shall be revocable at the pleasure of the person executing it.

Section 3. The fiscal year of the Society shall begin January 1.

Article X

AMENDMENTS

Proposals to amend this Constitution shall be made in writing to the Board of Directors and signed by at least ten active members; they shall reach the Secretary not later than February 1. The proposal, with the recommendations of the Board of Directors, shall then be presented to the Society at its annual business meeting. Approval shall require two-thirds majority vote of those in attendance. Final approval shall proceed through mail vote of membership, requiring a majority.

DIVISION NEWS

Electrodeposition Division

In accordance with the Bylaws of the Electrodeposition Division, Chairman M. L. Holt appointed the following committee to nominate officers for the period October 1954 to October 1956:

F. A. Lowenheim
E. H. Lyons
R. A. Woofter, *Chairman*

The above committee met May 4, during the Chicago Meeting and will submit to the membership in Boston the following slate of officers:

Chairman—Cloyd A. Snavely, Battelle Memorial Institute, Columbus, Ohio

Vice-Chairman—Sidney Barnartt, Westinghouse Research Laboratories, East Pittsburgh, Pa.

Secretary-Treasurer—Abner Brenner, National Bureau of Standards, Washington, D. C.

Members at Large on Executive Committee—These offices are normally assumed by the Division representatives on the Membership Committee and the Publication Committee. However, since the Publication Committee representative, Dr. Brenner, has been proposed as Secretary-Treasurer, the name of Dr. M. L. Holt, immediate Past Chairman, is proposed as a Member at Large.

R. A. WOOFTER,
Chairman, Nominating Committee

Electronics Division

The annual business meeting of the Electronics Division was held in Chicago on May 5.

The Chairman reported on the activities of the Division as follows.

The Division sponsored 5 symposia at the Chicago Meeting, comprising 72 papers on Luminescence, Instrumentation, Semiconductors, Phosphor Screen Application, and Refractory Metals and Compounds. The last named symposium was sponsored by the Rare Metals Group in cooperation with the Electrothermics Division.

The merger of the Rare Metals Group of the Division with the Electrothermics Division took effect following the Chicago Convention. Appropriate changes to the Division's Bylaws were adopted by letter ballot. The merger has been approved by the Board of Directors of the Society and the name of the new division has been changed to "Electrothermics and Metallurgy Division."

For the third consecutive year a booklet of enlarged abstracts has been printed and made available at $2.00 per copy. The demand for these booklets has increased steadily and it is expected that the 1954 edition of 500 copies will be disposed of before the close of the 1954–1955 year. A similar booklet will be published for next year's symposia.

The activity and interest of our members in the Semiconductor field has led to tentative planning for the formation of a Semiconductor Group as an integral part of the Division. This would fill the vacancy created by the loss of the Rare Metals Group. A committee, J. R. Musgrave, Chairman, H. R. Harner, and A. P. Thompson, will study the reorganization and draw up the necessary changes to the Bylaws for action at the business meeting next year.

Symposia planned for next year include: Luminescence, Semiconductors, Phosphor Application, and Oxide Cathodes.

The new officers of the Division elected at the business meeting are:

Chairman—Arthur L. Smith, RCA Victor Division, Radio Corporation of America, Lancaster, Pa.

Vice-Chairman (Luminescence)—Herbert Bandes, Sylvania Electric Products Inc., 35-22 Linden Place, Flushing, N. Y.

Vice-Chairman (General Electronics)—Arthur E. Middleton, P. R. Mallory & Company, Inc., 3029 East Washington Street, Indianapolis, Ind.

The present term of the Secretary-Treasurer has one more year to run.

The fiscal year of the Division continues until May 31. Also, the results of this year's sale of abstract booklets are not yet complete. Therefore, the financial report given below does not include data of this year's booklet sale.

Balance on hand, Jan. 1, 1953	$265.37
Net profit from 1953 booklet	219.27

Surplus from Social Hour, April 13, 1953	10.00
Interest on bank balance	8.02
Total assets	$502.66
Total paid out	58.00
Balance carried forward	$444.66

Charles W. Jerome
Secretary-Treasurer

Theoretical Electrochemistry Division

The program of the Theoretical Electrochemistry Division at the Chicago Meeting included a one day symposium on "Special Methods of Electrochemistry" and three general sessions. The symposium aroused much interest, and there was excellent participation of the audience during the discussion periods. Extended abstracts were made available thanks to the cooperation of Dr. E. Yeager of Western Reserve University.

Future symposia were discussed, and the topic of the next symposium was announced. This symposium, which will cover the "Fundamentals of the Electrochemistry of Batteries," will be held jointly with the Battery Division at the fall meeting in Boston. The suggestion was made that the Electrochemistry of Fused Salts be the topic of the symposium for the Spring meeting of 1955. A rapid survey of the members' opinions indicated a very favorable response to this suggestion.

Several problems pertaining to the organization of future symposia were discussed with the members of the Division. Suggestions to the officers of the Division on the following and other points would be welcomed: (*a*) usefulness of having a cycle of symposia in which given topics (electrode processes, electrolytes, electrokinetic phenomena, etc.) would be periodically reviewed; (*b*) organization of round-table discussions for topics which do not lend themselves to presentation to a large group; (*c*) planning of joint meetings with foreign organizations; (*d*) possibility of inviting foreign speakers; (*e*) usefulness of extended abstracts.

Paul Delahay,
Secretary-Treasurer

SECTION NEWS

Cleveland Section

The annual Cleveland Section Ladies' Night meeting was held on April 26 at Stouffer's Resturant in the new Westgate Center. Over 50 members and guests enjoyed a social evening and dinner together.

Dr. C. C. Rose of the Local Section presented an interesting talk entitled "Off the Beaten Path in the Southwest." His talk was well illustrated with many excellent colored slides obtained in his travels through the Southwest. A film, "Wildlife in Ohio," was also shown.

The results of the election of officers for 1954–1955 were announced as follows:

Chairman—Ernest B. Yeager, Department of Chemistry, Western Reserve University, Cleveland, Ohio

Vice-Chairman—W. H. Stoll, National Carbon Company, Box 6087, Cleveland, Ohio

Treasurer—Merle E. Sibert, Horizons Incorporated, 2891 East 79th Street, Cleveland, Ohio

Secretary—Karl S. Willson, General Dry Batteries Co., 13000 Athens Avenue, Cleveland, Ohio

The Cleveland Section sponsored a thirty-minute television program on May 2 over Station WNBK. A series of these programs is sponsored by the Cleveland Technical Societies Council and WNBK, with time allotted to the various member societies.

This year's program was arranged by Horizons Incorporated in cooperation with the Section Television Committee. E. Wainer and J. L. Wyatt represented Horizons, and P. S. Brooks is the Television Committee Chairman.

The series is entitled "Adventures in Science and Engineering," and has as its goal the stimulation of interest in the technical fields, particularly with respect to students. A local high school student is a guest on each program; the guest student was Charles Hanner of East Tech High School.

This particular program dealt with subjects of an electrochemical nature in which Horizons is actively engaged in research. These included Titanium Technology, the Metalphoto Process, Color Television, Aluminum Solders, and Electrostatic Printing. Participants included E. Wainer, F. C. Wagner, R. M. Gogolick, B. C. Raynes, E. F. Mayer, and J. L. Wyatt, all of Horizons Incorporated. Mr. Paul Bedford of the WNBK staff was announcer for the program.

The program was concluded with the presentation of prizes to the two winners of the Northeastern Ohio Science Fair. These awards went to Robert Chevako of Warrensville Heights Junior High School and Norman Thomas of Shaker Heights High School.

Merle E. Sibert, *Secretary*

Midland Section

Dr. Lee O. Case and Dr. Felix Rice, both from the University of Michigan, were guests of the Midland Section for dinner at the Midland Country Club on April 14.

Lee O. Case

Later in the evening, Dr. Case, who is Associate Professor of Chemistry at the University of Michigan, gave an interesting talk concerning his work with ultrasonics in electrochemistry.

A very elaborate, automatic, and precise apparatus has been assembled that will now give a tremendous amount of information with a minimum of effort. Dr. Case emphasized that the results are highly specific for various systems; he obtained voltage advantages of from 17 to 920 mv with his apparatus.

M. P. Neipert,
Secretary-Treasurer

Philadelphia Section

Members and guests of the Philadelphia Section and their wives gathered for the final meeting of the season on the beautiful campus of Bryn Mawr College on May 15. All told there were 46 persons present. A cocktail hour, followed by dinner, was held at the Deanery. After dinner the group strolled over to the lecture hall of the Chemistry Department for the evening program. The speaker was Mr. George A. Perley, Associate Director of Research of the Leeds and Northrup Company. Mr.

Perley, a member of the Local Section, has made significant contributions to the field of electrochemical instrumentation. However, on this occasion he talked about two of his hobbies—the study of natural history and photography. He showed first a color film of a trip made last summer through several of the national parks in the West. Outstanding among the numerous beautiful "shots" were pictures of birds at the Utah Bear River Migratory Bird Refuge. Mr. Perley also showed a remarkable color film of the blooming of flowers taken by the time lapse technique in his own home and in large part with equipment of his own construction. Mr. Perley has become widely known for his nature talks and films, and the group found his presentation most enjoyable.

This pleasant meeting was made possible largely by the generous cooperation of Dr. Ernst Berliner and other members of the Bryn Mawr staff, and to them the Philadelphia Section is very grateful.

The Nominating Committee, at the March meeting, presented the names of the incumbent officers for re-election to office next year and provision was made for additional nominations from the floor at the May meeting. The present officers were re-elected at this time.

George W. Bodamer, *Secretary*

NEW MEMBERS

In April 1954 the following were elected to membership in The Electrochemical Society:

Active Members

John C. Devins, General Electric Research Laboratory, mail add: 17 Birch Lane, Scotia, N. Y. (Electric Insulation)

Frederick R. Duke, Iowa State College, Dept. of Chemistry, Ames, Iowa (Theoretical Electrochemistry)

James E. Fritts, Ternstedt Division, General Motors Corp., 6307 W. Fort St., Detroit, Mich. (Electrodeposition)

Peter Kabasakalian, Schering Corp., 86 Orange St., Bloomfield, N. J. (Electro-Organic)

Layton C. Kinney, Armour Research Foundation, mail add: 10 W. 35 St., Chicago, Ill. (Industrial Electrolytic)

Rudolf W. Knoepfel, North American Solvay, Inc., 50 Broadway, New York, N. Y. (Industrial Electrolytic)

Sidney H. Liebson, U. S. Naval Research Laboratory, Solid State Div., Code 6450, Washington, D. C. (Electric Insulation, Electronics, Theoretical Electrochemistry)

Wesley G. Nilson, Ebasco Services Inc., 2 Rector St., New York, N. Y. (Corrosion)

Juan Manuel Nordemann, Manuel Guelfi & Cía, S. A., Av. Agraciada 1777/89, Montevideo, Uruguay (Battery and Electrodeposition) Formerly Associate Member

Vincent P. Pearson, Inland Steel Co., mail add: 614 So. Park Drive, Chesterton, Ind. (Electrodeposition)

Richard H. Pfost, Atlas Supply Co. Laboratory, 226 Mt. Pleasant Ave., Newark, N. J. (Battery)

Herman S. Preiser, Dept. of the Navy, Bureau of Ships, mail add: 1702 Summit Place N. W., Washington, D. C. (Corrosion)

S. K. Ramaswamy, Messrs. Lever Brothers (India) Ltd., mail add: H.V.M. Factory, P. O. Box 70, Tiruchirapalli, India (Industrial Electrolytic)

John Rehner, Jr., Standard Oil Development Co., mail add: 200 Linden Ave., Westfield, N. J. (Corrosion, Theoretical Electrochemistry)

John C. Russell, Rhoanglo Mines Service, Research & Development Div., P. O. Box 172, Kitwe, North Rhodesia (Industrial Electrochemistry)

Patricia Ann Welch, General Electric Co., mail add: 4855 W. Electric Ave., Milwaukee, Wis. (Electronics)

Associate Members

Andrew Glovatsky, Sylvania Electric Products Inc., mail add: 137 W. 5 St., Emporium, Pa. (Electrodeposition)

John L. Griffin, University of Michigan, mail add: 534 N. Main St., Ann Arbor, Mich. (Theoretical Electrochemistry)

Jamshed Mathur, Imperial Chemical Industries, mail add: I. C. I. Ltd., Crescent House, Ballard Estabte, Bombay, India (Industrial Electrolytic, Electro-Organic, Electrodeposition)

Jacob M. Miller, Armour Research Foundation, Technology Center, Chicago, Ill. (Corrosion, Theoretical Electrochemistry)

Ramesh Chander Misra, Defense Ministry, Government of India, Technical Development Establishment, mail add: Shri P. L. Misra, % Surveyor General's Office, Dehra Dun, India (Battery, Industrial Electrolytic, Theoretical Electrochemistry)

Student Associate Members

Milton B. Clark, Western Reserve University, mail add: 3111 Mapledale Ave., Cleveland, Ohio (Theoretical Electrochemistry)

Joseph S. Dereska, Western Reserve University, mail add: 20703 Clare Ave., Maple Heights, Ohio (Theoretical Electrochemistry)

Warren H. Krause, Service Recorder Co. Inc., mail add: 3802 Woburn Ave., Cleveland, Ohio (Electronics)

Resignations

J. C. Langford, 2240 Sun Life Bldg., Montreal, Que., Canada

K. E. Luger, 2716 Danville St., Houston, Texas

A. B. Oatman, National Carbon Co., 30 E. 42 St., New York, N. Y.

G. W. Slomin, 3151 Clairmont Drive, San Diego, Calif.

PERSONALS

Jackson Burgess has been elected Chairman of the Board of Directors of the Burgess-Manning Company, Libertyville, Ill.

Myron B. Diggin, Hanson-Van Winkle-Munning Company, Matawan, N. J., has been appointed assistant vice-president. In his new assignment, he is expected to devote more time to the specific development and use of H-VW-M electrochemical processes. Mr. Diggin will continue as technical director of the company.

Erwin F. Lowry, manager of the Lighting Engineering Laboratories, Sylvania Electric Products Inc., Salem, Mass., has been named to receive the 1954 Gold Medal of the Illuminating Engineering Society. This medal, the highest honor in the field of illumination, is awarded for meritorious achievement, conspicuously furthering the profession, art, or knowledge of illuminating engineering.

George A. Perley, associate director of research, recently celebrated the 25th anniversary of his employment by Leeds & Northrup Company, Philadelphia, Pa. President I. Melville Stein presented him with an anniversary plaque.

G. Stuart Krentel, formerly plating salesman with the Electroplating Equipment and Supply Division of A. J.

Lynch Company, Los Angeles, Calif., became a member of the staff of Hanson-Van Winkle-Munning Company when that company purchased the plating division of the Lynch Company. Mr. Krentel will continue to cover Los Angeles.

E. C. LARSEN, previously chief engineer, Tungsten and Chemical Division, Sylvania Electric Products Inc., Towanda, Pa., is now associated with the J. T. Baker Chemical Company, Phillipsburg, N. J.

WILLIAM BURTON LLOYD has transferred from Edgewater Works, National Carbon Company, Cleveland, Ohio, to the company's Asheboro, N. C., plant.

WILLIAM ALFRED LALANDE, JR., was elected vice-president of the Pennsylvania Salt Manufacturing Company, Philadelphia, Pa. He will continue as manager of research and development of the company in addition to his new responsibilities.

ERWIN SOHN

Erwin Sohn, a member of The Electrochemical Society, died on May 5 after a short illness. He was 67 years old.

Mr. Sohn, at the time of his death, was connected with the Eagle-Picher Research Laboratories, Joplin, Mo. Earlier he had been a Research Fellow at Mellon Institute; then he joined the Standard Sanitary Manufacturing Company, Louisville, Ky., where he was director of research for many years. Later he became director of research for the National Sanitary Company, Salem, Ohio, leaving them in 1952 to join the Eagle-Picher organization.

Mr. Sohn became a member of The Electrochemical Society in 1926. He was also associated with several other technical societies, including the American Ceramic Society, the American Chemical Society, the American Electroplaters' Society, the American Society for Testing Materials, and the American Institute of Mining and Metallurgical Engineers. His specialty was ceramic coatings for metals and the problems involved in applying these coatings.

RECENT PATENTS

Selected by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette.

April 6, 1954

Crafts, W., 2,674,529, Manufacture of Low-Carbon Stainless Steel

Rassbach, H. P., 2,674,530, Manufacture of Low-Carbon Stainless Steel

Prosen, E. M., 2,674,571, Method of Electropolishing Dental Appliances

Gundel, W., and Scherff, W., 2,674,572 Production of Tetrachloro-Cyclohexanones

Crauland, J. J. L., 2,674,573, Process for the Preparation of Substituted Alkanes

Stevenson, C. H., 2,674,638, Induction Metal Melting Furnace

Stevenson, C. H., 2,674,639, Method of and a Furnace for Induction Melting Metal

Tama, M., 2,674,640, Apparatus for Dispensing Molten Metal

Holmes, G. I., 2,674,641, Thermoelectric Generator and Method for Production of Same

Agruss, B., and Finan, F. B., 2,674,642, Storage Battery Active Material

Dahl, K. E., and Hoiby, J. C., 2,674,643, Battery Thermostat

April 13, 1954

Cusano, D. A., and Studer, F. J., 2,675,331, Transparent Luminescent Screen

Lowenheim, F. A., 2,675,347, Plating of Tin-Zinc Alloys

Greenspan, L., 2,675,348, Apparatus for Metal Plating

Capita, E. R., 2,675,414, Induction Furnace

Ray, W. A., 2,675,416, Radiation Thermocouple

Heibel, J. D., 2,675,417, Pyroelectric Device

Nichols, H. B., 2,675,418, Electric Storage Battery and Process of Manufacture

Godshalk, J. B., 2,675,522, Method and Apparatus for Testing Storage Batteries

LITERATURE FROM INDUSTRY

ELECTRODES AND ELECTRODE ASSEMBLIES. A new catalogue describing "pH Electrodes and Electrodes for Measuring Redox Potentials—Assemblies, Parts and Accessories" has been published. This book covers the complete L & N electrode line, chemicals for electrode servicing, and auxiliary electrode equipment, such as clamps, holders, thermometers. Primarily, however, it is designed to present electrode assemblies for measurement, recording, and/or control of solution pH and redox potentials, and should be of major interest to production and research men engaged in this work. Leeds & Northrup Co. P-217

SANTICIZER 141. A revised and expanded technical bulletin on Santicizer 141, an alkyl aryl phosphate nontoxic, primary plasticizer for polyvinyl chloride and its copolymers, as well as other important commercial resins, is available on request. The bulletin contains comparative performance evaluation data, suggested formulations employing the material and a summary of the extensive toxicity work conducted on the plasticizer. Also discussed are other properties which Santicizer 141 imparts to formulations, such as low temperature flexibility, grease resistance, and heat sealability, as well as high tensile and tear strength. In many applications, its excellent resin solvency makes possible savings in time, heat, and power. Monsanto Chemical Co. P-218

AIRBLASTING AND SANDBLASTING NOZZLES. New catalogue covers the manufacturer's line of airblast cleaning nozzles. Three standard models of nozzles are described. Also included are pressure blast hose fittings for standard airblast nozzles. Of special interest to cleaning engineers is the description of materials employed in the nozzles, and the discussion of how to control compressed air consumption. This is accompanied by tabular data showing the importance of controlling nozzle wear. American Wheelabrator & Equipment Corp. P-219

TITANIUM TUBING. Properties, applications, and advantages of titanium tubing are presented in a new bulletin. Some of the research and development which went into the product is outlined, together with the properties of titanium which make it a promising material for many new applications. Tube sizes of seamless titanium and WEL-DRAWN titanium are listed. Tubing tolerances, chemical analysis, and finishes are other topics discussed. An interesting and informative section is written on processing and fabricating characteristics of titanium tubing. Superior Tube Co. P-220

TEFLON PACKINGS FOR VALVES AND PUMPS. Recently issued catalogue on the manufacturer's "Chemiseal" valve and pump packings features advantages of Teflon as a packing material—its chemical resistance, noncontamination, and extreme anti-hesiveness. Illustrated and described with easy reference selection tables are V-Type, Cup-and-Cone Type, and Wedge Type Valve packings; and three types of pump packing rings—pure Teflon, Teflon with mica, and Teflon with graphite. United States Gasket Co. P-221

"Hilger Equipment for Raman Spectrography." 20-page catalogue illustrates and describes in detail the E612 Hilger Two Prism Glass Raman Spectrograph, which may be used in photographic work or as a direct reading instrument, and the E517 and E518 Spectrographs which are lower cost instruments for use with Raman Spectra or for spectrographic recording of other low intensity sources. The high reproducibility and resolution of the instruments are revealed in the several photographs of recorded traces which are shown. The Hilger Raman Source FL-1, and the control units, cameras, oscillators, amplifiers, and other complementary and accessory equipment are also illustrated and described. Hilger and Watts Ltd. P-222

NEW PRODUCTS

Butyl-Molded Miniature Transformer. New butyl-molded miniature current transformer features both window-type and bar-primary construction. Designated the JCA-O current transformer, the product is designed for operating meters and instruments and can be used on either single-phase two-wire or polyphase circuits. It is rated at 600 volts and is suitable for use on any circuit of 600 volts or below. Two current ratings are available in both the window and bar-primary models; these are 200:5 and 400:5 amperes. The product's molded butyl serves as insulation and support and casing. It provides high dielectric strength, excellent heat-dissipating properties, and resiliency, and resists oxidation, arc-tracking, and moisture. General Electric Co. N-86

Alkaline Cleaner for Spray Washers. A new alkaline cleaner, which is entirely free of caustic soda, has been developed for use in mechanical spray washers prior to phosphate coating. By eliminating caustic soda, the crystalline structure of the phosphate coating is made much finer and more effective. This product may be used at varied concentrations and temperatures for the removal of oils and greases from fabricated parts prior to subsequent operations. The concentration of this cleaning compound is entirely dependent upon the type and degree of soil involved. Detrex Corp. N-87

Polyethylene Flashlight Case. A case which overcomes corrosion, the major problem of flashlight users, is being molded of "Alathon" polyethlene resin. The use of this material has made it possible for the flashlight to remain unaffected by moisture even when submerged. "Alathon" is very light weight and yet so tough that the manufacturer guarantees the case unconditionally against breakage. Gits Molding Corp. N-88

Selenium Rectifiers. An exceptionally fine series of miniature selenium rectifiers for electronic equipment requiring a load current of 50 ma or less is now in quantity production. The "CR" series of miniature rectifiers consists of a number of selenium cells assembled within a cylindrical aluminum housing. Their small compact size makes them ideal for original equipment manufacturers of TV boosters and UHF converters or for replacement of rectifiers when servicing these sets. Equally useful for experimental devices and electronic equipment having relatively low current drain. International Rectifier Corp. N-89

Zirconium Oxide. Production of pure (monoclinic) zirconium oxide has been announced. It is useful where extreme purity is required for chemical reactions. It is the starting material for all zirconium chemicals. Its monoclinic structure gives it sharper edges making it an ideal polishing agent. Also useful as a pigment in plastics, ceramics, glasses, and paints. It is claimed that this pure oxide will have the finest grain size available. Recent spectrographic analyses show it to be 99.2% pure. Zirconium Corp. of America. N-90

Magnetic Stirrer. A new stirrer, known as the "Lew" Magnetic Stirrer, has been designed for vacuum, pressure, or atmospheric work. Liquids up to a consistency of glycerin can be agitated. The design is unique in that the powerful magnetic field is located above the vessel proper, leaving the underside entirely free for the application of heat or cold. Two models are available. The Vacuum and/or Pressure Model has a side connection, the Atmospheric Model does not. Either model may be provided with 6-pole or 8-pole dual magnets. The 6-pole type is for laboratory use; the 8-pole type is intended for pilot-plant work. Scientific Glass Apparatus Co. Inc. N-91

ADVERTISERS' INDEX

Pocket Comparator. 1½ in.-diameter "Indeco" pocket comparator with six-power magnifying lens measures angles, small diameters and radii, and microscopic lengths directly through glass-inscribed reticle. Measurements of tool wear, chamfer angles, small part tolerances, etc., are made quickly on the "Indeco" without refocusing. Comparator is placed in contact with part to be measured and dimension is lined up with reticle for immediate, accurate check. International Development Co. N-92

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Please address replies to box shown, ℅ The Electrochemical Society, Inc., 216 W. 102nd St., New York 25, N. Y.

Position Wanted

Electrometallurgist. B.S., M.S., and Ph.D. degrees in metallurgy. Permanent resident alien. Eight years in nonferrous and corrosion research. Knowledge of corrosion, hydro- and electrometallurgy, radiography, x-ray diffraction, spectro-analysis, and heat treatment. Desires position in research, production, or plant control with opportunity for experience and advancement. Location immaterial. *Reply to Box 355.*

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International Nickel Company, Inc., New York, N. Y. (3 memberships)

Kaiser Aluminum & Chemical Corporation, Division of Metallurgical Research, Spokane, Wash.

Mathieson Chemical Corporation, Niagara Falls, N. Y.

McGean Chemical Company, Cleveland, Ohio

Merck & Company, Inc., Rahway, N. J.

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