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VOL. 102 • NO. 3

CONTENTS

Editorial

Revolution in Mathematics. *C. O. Oakley*..... 55C

Technical Papers

- ✓ Resistance and Polarization in a Storage Battery. *E. Willihnganz*..... 99
- Galvanic Corrosion Behavior of Titanium and Zirconium in Sulfuric Acid Solutions. *David Schlain, Charles B. Kenahan, and Doris V. Steele*..... 102
- Electrodeposition of Cellulose. *C. L. Mantell and Frank Cozzarelli*..... 110
- The Electrolytic Reduction of Isobutyraldehyde in Acid Solution. *Sherlock Swann, Jr., E. I. Onstott, and F. H. Baastad*..... 113
- Determination of Hydrogen in Titanium. *T. D. McKinley*... 117
- ✓ Influence of Impurities in the Electrolyte in Chlorine-Caustic Electrolysis by the Mercury Cell Process, IV. Investigation of the Influence of Metals on the Cathodic Current Efficiency. *Gösta Angel, Tage Lundén, Stig Dahlerus, and Rolf Bärnland*..... 124
- ✓ Electrochemical Behavior of a Titanium-Fused Salt-Platinum Cell. *M. E. Straumanis and A. W. Schlechten*..... 131
- ✓ The Extractive Metallurgy of Zirconium by the Electrolysis of Fused Salts, III. Expanded Scale Process Development of the Electrolytic Production of Zirconium from K_2ZrF_6 . *Bertram C. Raynes, Edward L. Thellmann, Morris A. Steinberg, and Eugene Wainer*..... 137
- Conductances, Viscosities, and Densities of Solutions of Potassium Thiocyanate in Methanol at Temperatures within the Range 25° to -50°C. *Paul G. Sears, Richard R. Holmes, and Lyle R. Dawson*..... 145

Current Affairs

- Cincinnati Meeting, May 1 to 5, 1955..... 57C
- Bylaws of The Electrochemical Society..... 60C
- News Items..... 59C Personals..... 68C
- Division News..... 64C Book Reviews..... 68C
- Section News..... 65C Literature from Industry.. 68C
- New Members..... 67C New Products..... 69C

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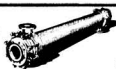
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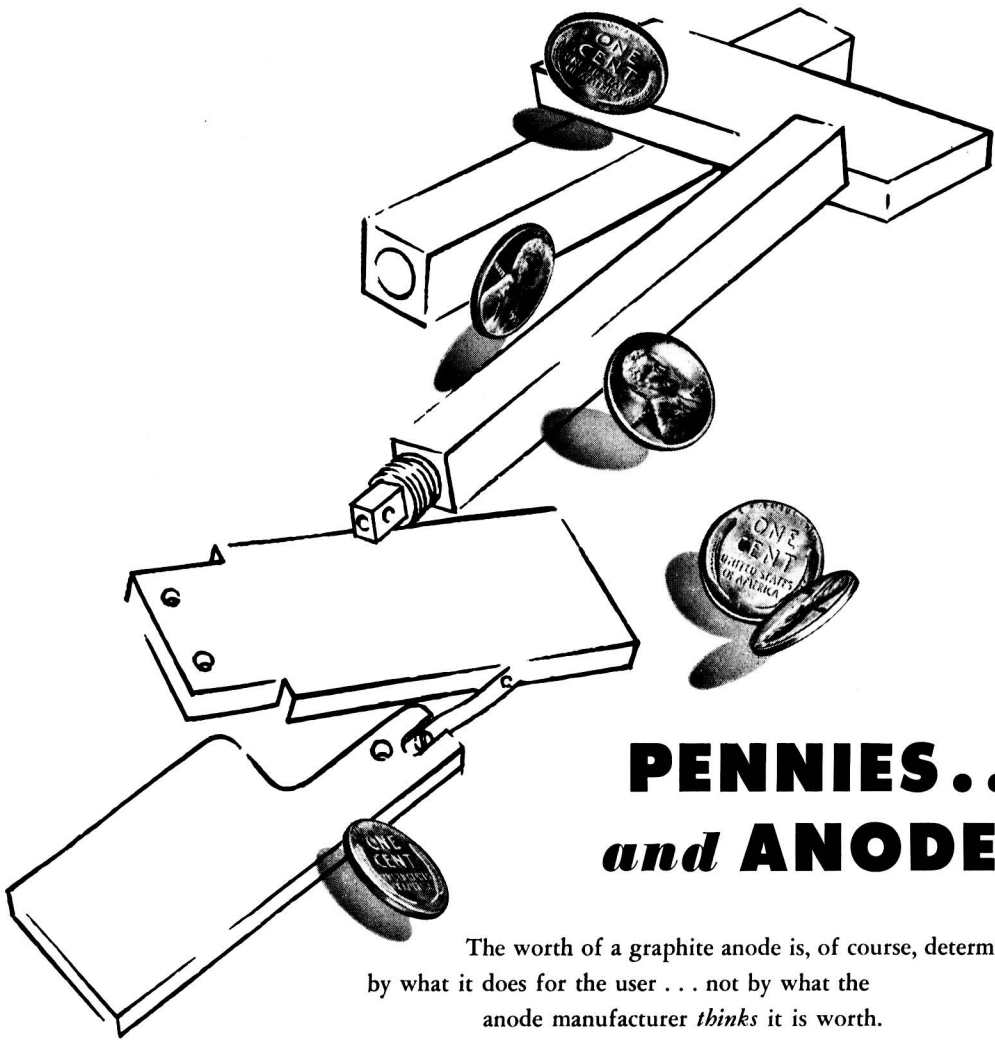
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Revolution in Mathematics

THERE IS A REVOLUTION taking place in mathematics—in the kinds of mathematics which are now being offered in high schools and colleges. Essentially, this revolution is the result of new and ever increasing demands placed on mathematics by all of the sciences.

A recent editorial in this JOURNAL (Vol. 101, No. 11) discussed the crisis in science teaching—and a crisis it is, indeed. As a teacher of mathematics in a small college, I wish that each member of The Electrochemical Society could be made to realize just how serious the situation is because I believe that then you would do something about it. What I have to say relates to this problem, but only with respect to mathematics. My concern is with the fields of mathematics being taught rather than with the teaching of mathematics.

Let me say in the beginning that I am not considering the low level to which mathematics has fallen in certain high school curricula. This is certainly an alarming phase and sometime in the past could have been thought of as a revolution in itself. I am hopeful, however, that it will turn out to be no more than a temporary rebellion. There are signs that some good high schools and private schools are revising their mathematical offerings upward and in a very modern way.

What I want to point out is that there are recent developments which may save the day for mathematics and for science in general. In order that we may see the changes in proper perspective, we should take a quick look at the rate at which the total body of mathematics is growing. It does not require the assistance of a giant computer for us to realize that more mathematics has been produced since 1900 than in all previous time. Furthermore, unlike some disciplines, mathematics rarely, if ever, discards a theory as being “wrong” or useless. Theories come and theories go in other areas of human endeavor, but in mathematics they come and stay. Once a theorem, always a theorem is the rule, and it appears that mathematical knowledge grows exponentially.

Now consider what most high schools have been teaching for many decades. These are: *arithmetic*—mostly by rote; *algebra*—a minimum of, and with few general unifying principles; *plane geometry*—but less and less by the deductive method; *solid geometry*—some, perhaps, but almost wholly intuitional; *trigonometry*—mostly numerical—and when did you last solve a triangle by logarithms?; *business mathematics*—the less said the better.

This fine old classical program must become more elastic. The basic material in it is as beautiful as ever, but in this modern day and age there simply is no time to dwell upon it at such length. It is a painful process to trim it, but this must be done in order to get on with more recent areas of mathematics. This is being done quite successfully in scattered sections of the country. As much as one full year of analytic geometry and calculus is now offered in the better schools in the nation.

(Continued on next page)

Editorial (*continued*)

Some even offer work in elementary mathematical logic and statistics. The University High School in Urbana, Ill., is in the process of writing its own text material in which true integration of algebra, geometry, trigonometry, analytic geometry, and elementary calculus is accomplished. This is indeed a notable advance.

In the first two years most colleges have been teaching: *trigonometry*—still too much numerical work and not enough analytical; *algebra*—but very little abstract material; *analytic geometry*—17th Century; *calculus*—18th Century at the latest. And *this* program also has to become more elastic. Again, there is insufficient time. This program brings us—at the end of the sophomore year—up to something like the year 1755, to make it an even 200 years ago. The junior who takes differential equations and advanced calculus hardly gets into 19th Century mathematics. And the prospective engineer, if his college program permits, may take one more course in mathematics to bridge the gap of a century and a half! Then this underdone mathematical product is turned out to begin his life work of engineering service to the sciences in this very modern world.

Gentlemen, I apologize for the product; that it is so poor is not your fault. I place the blame squarely upon my own shoulders and those of my fellow mathematicians, because in the past we have had the student for four college years and during that time we have elected to give him practically no mathematics developed in the last century.

But right here is where the good news of the revolution comes in. Now there are more and more colleges which are trying to do something about this intolerable situation. While still giving an adequate amount of time to the classical mathematical material up to and including the calculus, they are paying careful attention to the needs of modern science and engineering. Undergraduates in many colleges¹ over the country are learning something about symbolic logic, group and matrix theory, Boolean algebra, linear programming, game theory, probability, statistics, etc. Many of these subjects have already proved even more valuable than “the calculus,” especially in such areas as operations analysis, computer theory, circuit design, quality control, theory of communication, and even actuarial mathematics.

The revolution in mathematics may be bloodless, but it is not painless. It is, indeed, painful for some teachers of mathematics to give up what they have always considered necessary and to replace this by less familiar material even though the evidence is before them that the new ideas are needed for modern science. It can only be hoped that the revolution will spread and that more colleges and universities will include modern mathematical theories along with the essential parts of the classical in their undergraduate programs. For only thus can they help the youth of the nation keep abreast of current developments in the sciences.

—C. O. OAKLEY²

¹ Having experimented at Haverford for the past seven years with a Freshman course containing some modern mathematics, we are convinced that we have improved our end product.

² Professor Oakley is head of the Department of Mathematics in Haverford College, Haverford, Pa.—*Ed.*

Resistance and Polarization in a Storage Battery¹

E. WILLIHGANZ

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ABSTRACT

The electrical resistance of one cell of a 100 amp-hr automobile type storage battery has been studied by the a-c bridge method at 30–16,000 cycles. Results can be explained by considering the battery as a source of potential in series with a resistance, a capacitance, and an inductance. The inductance is only a fraction of a microhenry. Apparent values of the resistance and capacitance vary with frequency. At 1000–3000 cycles the apparent resistance is about one milliohm, but at 60 cycles it is 10–20% higher. The apparent capacitance is 15–20 Farads at 60 cycles and becomes too small for measurement at 1000 cycles. Attempts to explain these results show a step in the electrochemical reaction which has not been recognized previously and which requires further study.

INTRODUCTION

The high rate performance of a battery depends to a large extent on its internal resistance. This resistance is particularly important when a voice frequency is passed through a battery in a telephone exchange, or when a short pulse of current is used to operate a switch in a central power station.

Earlier work (1) indicated that the resistance could be measured by a bridge using 3000 cycle alternating current. This high frequency was chosen to eliminate polarization, that is, to prevent chemical effects from building up a counter emf which could be confused with that due to electrical resistance. In subsequent work it was observed that there was polarization in measurements at lower frequencies. The bridge was modified, therefore, to study this polarization.

Bridge measurements of lead batteries have been made by Kluck (2) and resistance measurements using pulses of direct current have been made by Lander (3). These workers were interested in the electrical resistance, rather than polarization. The general problem of electrode polarization has been reviewed by Grahame (4, 5) and pertinent studies of the lead electrode have been made by Baars (6) and by Falk and Lange (7).

EXPERIMENTAL

The battery used for this work was a single cell from a 100 amp-hr automobile cranking battery of conventional construction. The bridge was similar to that used previously (1) except for the presence of an adjustable condenser in series with the adjustable resistor of the bridge arm adjacent to the battery being tested. The null indicator was a cathode ray oscillograph. This gave excellent sen-

sitivity at high and low frequencies and permitted the unbalanced portion of the battery output voltage to be photographed and studied.

Exploratory tests showed that the bridge balance was practically complete at each frequency, and was independent of current in the range 0.1–5 amp. At frequencies of 3000–16,000 cycles results appear unreliable. Effects of stray capacitance and inductance were clearly evident, and it also appeared possible that inductive effects caused the current distribution to be nonuniform within the cell. Therefore, only the low frequency results are discussed. In this range of frequencies, the apparent inductance was constant and equal to that of a copper rod about 4 in. long. Since this is very nearly the distance between cell terminals, it is considered to have no chemical significance.

When both electrodes were lead dioxide, the apparent resistance was independent of the frequency, and no capacitance was needed in the bridge to get a good balance. However, when sponge lead electrodes were used, there was a considerable variation with frequency of both the measured resistance and capacitance (see Fig. 1). It is concluded, therefore, that in an ordinary battery, the variation with frequency occurs exclusively at the lead-acid interface, and not at the lead dioxide surface.

The electrochemistry of the lead-acid interface was also studied by passing short pulses of direct current through the bridge circuit after removing all condensers from the current path. The current pulse was obtained by putting a half wave rectifier in series with a 60 cycle current source and connecting enough batteries in opposition to block all but the current peaks. The bridge was balanced to eliminate the first portion of the battery voltage pulse, and the residual voltage delivered by the bridge circuit was photographed. Fig. 2A shows a current pulse of 1.75 amp peak, Fig. 2B shows the battery output

¹ Manuscript received September 10, 1954. This paper was prepared for delivery before the Boston Meeting, October 3 to 7, 1954.

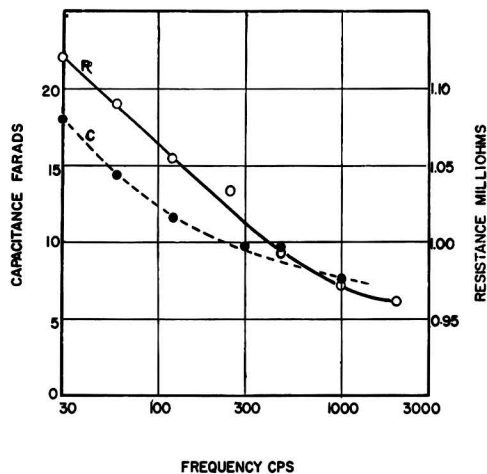


FIG. 1. Typical bridge results

voltage pulse of approximately 1.75 millivolts peak, while Fig. 2C shows the bridge output of approximately 0.2 millivolts which corresponds to a battery voltage of 0.5 millivolts.

This pulse was next studied by varying the concentration of lead ions in solution. This was done by superimposing a steady direct current bias on the pulsed current passing through the bridge. The effect of this bias on a charge pulse is shown in Fig. 2D, 2E, and 2F for bias values of 2.5, 0, and -25 amp. Similar results for a discharge pulse are shown in Fig. 2G, 2H, and 2I. In each of these figures three separate lines are shown. There is the voltage across the battery to show the size and position of the current pulse; there is the bridge output at a

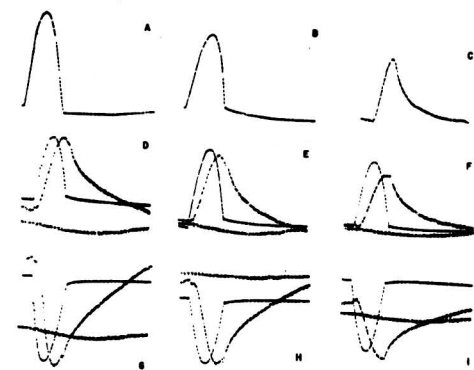


FIG. 2. Oscillograms using 60 cycle pulsed d.c. A, current; B, battery voltage; C, bridge output voltage (nonohmic overpotential); D, charge pulse and 2.5 amp d-c charge; E, charge pulse, no steady d.c.; F, charge pulse, 25 amp d-c discharge; G, discharge pulse, 2.5 amp d-c charge; H, discharge pulse, no steady d.c.; I, discharge pulse, 25 amp d-c discharge.

sensitivity 10 times as great; finally there is the residual hum. Fig. 2B and Fig. 2C can be used to identify the battery voltage and bridge output in these patterns.

The battery used for this test was first kept for one week on a low rate charge to remove all soluble lead compounds. This charge was continued while Fig. 2D and 2G were prepared. It is assumed that the lead-acid interface was free of lead ions.

The battery was then given a 25 amp discharge for 5 min and allowed to stand on open circuit for several hours. Fig. 2E and 2H were then made. It is assumed that during this test the acid at the interface was practically saturated with lead sulfate.

Finally the battery was discharged at 25 amp while Fig. 2F and 2I were made. It is assumed that during this test the electrolyte was supersaturated with lead sulfate.

DISCUSSION

The lead ion concentration during these tests can be calculated using the Nernst equation. The 0.1 v polarization during charge and the -0.1 v polarization during discharge indicate a difference in lead ion activity of more than one million times, but the difference in the voltage pulse is barely measurable. This is difficult to explain unless the primary battery reaction does not involve lead ions. Normal battery operation is difficult to explain without involving lead ions, so that battery reactions apparently consist of two steps, the first of which does not involve lead ions at the sponge lead surface.

Another aspect of this reaction is indicated by using the data of Falk and Lange (7) who observed that in sulfuric acid at 1000 cycles lead has a capacitance of 12 microfarads/cm². Under the same conditions, the battery used here had a capacitance of 6 Farads and, therefore, should have an interfacial area of 500,000 cm². This number appears consistent with the particle size of sponge lead observed under the microscope. The current pulse of 1.25 amp average for 0.0044 sec gives a charge of 0.005 amp-sec or 0.01 microcoulombs/cm². To deposit a monolayer of hydrogen with a spacing of 5°A would require 64 microcoulombs/cm². Consequently, the test pulse corresponds to only a small fraction of a monolayer, and probably only a small fraction of the charge of the double layer. There is considerable uncertainty in the estimated area of the interface, but this should not invalidate the conclusion that the current pulse causes only a minor disturbance to the composition of the double layer.

The decay process explains, electrically at least, the results of the a-c bridge measurements. At 60 cycles the measured capacitance includes a considerable amount of pseudocapacitance as defined

by Grahame (5), while the high apparent resistance is clearly the result of energy dissipated by the decay process, and is believed to correspond to his polarization resistance.

There is no evidence for an activation overpotential in these measurements. Such an effect could be present and pass unnoticed if this potential were proportional to the current in the range studied. It would thus show up electrically as an additional resistance on the lead surface. Such a film was not mentioned by Falk and Lange (7) whose experimental apparatus should have shown it had it been present.

Accordingly, it is concluded that the nonohmic overpotential produced during these tests involves only a change in the composition of the double layer and its subsequent decay. The nature of this decay reaction requires further study.

Resistance values assigned to a battery depend

on the contribution of the decay process to the bridge readings at the test frequency. At 1000 cycles it is estimated that the error amounts to about 1%. However, to avoid ambiguity it is desirable to specify the test frequency whenever a battery resistance is mentioned.

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

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Galvanic Corrosion Behavior of Titanium and Zirconium in Sulfuric Acid Solutions¹

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ABSTRACT

Aluminum alloys are the anodic members of titanium-aluminum alloy couples in dilute sulfuric acid solutions in the presence of air. In stronger acid solutions, particularly when air is absent, aluminum alloys are anodic only at the beginning of the immersion period. After an induction period titanium becomes anodic. Aluminum alloys are always anodic in zirconium-aluminum alloy couples immersed in sulfuric acid solutions. The rate of galvanic attack increases with the supply of air. The direction of flow of the galvanic current is always in agreement with the relative values for the electrode potentials of the single metal specimens. Little, if any, galvanic corrosion occurs in couples of titanium or zirconium with stainless steel, although there are generally sizeable differences of potential between single specimens of these metals. In solutions in which single specimens of titanium are inert and cathodic with respect to aluminum alloys, contact with these alloys may cause titanium to corrode. This is attributed to activation of titanium surfaces by the hydrogen evolved. Contact with stainless steel in solutions in which titanium is the anodic member of the couple results in marked decreases in corrosion rates of titanium because of anodic polarization of titanium surfaces.

INTRODUCTION

A knowledge of the galvanic corrosion properties of titanium and zirconium is essential because of the growing industrial importance of these metals and the probability that they will be used in structural contact with other metals under corrosive conditions. The present investigation includes a study of the behavior of titanium and zirconium in contact with aluminum alloys or 18-8 stainless steel in several concentrations of sulfuric acid. These alloys are not only common structural materials but, upon dissolution, may form cations known to have pronounced effects on the electrode potentials and corrosion rates of titanium in acid solutions (1, 2). Since titanium surfaces are passivated by the presence of air (3, 4), various types of aeration were used in these experiments.

EXPERIMENTAL METHOD

All experiments were done at 35°C, and generally lasted 15 days. Some were carried out in stoppered bottles with a constant flow of air or helium, others in loosely covered vessels with no forced gas flow. In stoppered-bottle tests, gas was passed through the solution for about 1 hr before immersion of the metal specimens and continuously throughout the experiment. Rates of flow, measured with rotameters, were approximately 50 ml/min. Helium was passed

through a water bottle and several spray traps before entering the experimental train. Air was passed through an additional bottle containing sodium hydroxide solution. When acid was consumed rapidly as a result of the corrosion process, the solution was replaced with fresh solution at suitable intervals. Evaporation from loosely covered vessels was compensated for by adding distilled water. The acid concentration was generally maintained within a range of 0-20% of the nominal value.

Table I gives the composition of titanium and zirconium specimens; other metals used were standard commercial products. All specimens were given a preliminary polish with wet silicon carbide paper on a mechanical polisher. Just prior to immersion they were surfaced by hand with dry 3/0 emery cloth, rubbed with wet pumice, washed with water, dried with acetone, and weighed. Specimens were never reused. C. P. chemicals, distilled water, and Grade A helium (99.9 + % pure) were used. The number of experiments carried out for each set of conditions varied from one to six.

Two types of galvanic-couple experiments were used. One, the "open" couple, is a modification of one described by Fraser and his coworkers (5). Fig. 1 shows the apparatus used in experiments with stoppered bottles. The large bottle contained two specimens of each of the two metals involved in the experiment and approximately 550 ml of solution. The metal specimens were 0.13 cm thick, 0.64 cm

¹ Manuscript received June 8, 1954. This paper was prepared for delivery before the Wrightsville Beach Meeting, September 13 to 16, 1953.

TABLE I. Analysis of titanium and zirconium

	C	N ₂	O ₂	Fe	Mg	Mn	Cr	Ni	W	Cu	Si	Cl	Hf
Titanium ^a	0.044	0.027	0.1 ^c	0.13	0.013	0.076			0.02 ^c max		0.04 ^c max		
Zirconium, high purity ^a	0.02	0.04	0.09	0.05					0.001	0.005			0.20
Zirconium, low purity ^b	0.38	0.045	0.1 ^c	0.74	<0.01		0.042	<0.01			0.03	0.02	1.65

^a Consolidated by arc-melting, 20% cold rolled.

^b Annealed in vacuum at 800°C for 2 hr.

^c Nominal value, not based on an actual analysis of the metal used.

wide, and 15.3 cm long. The upper portion of each specimen was insulated with plastic cement, leaving 7.6 cm of length exposed to the solution (area, 0.12 dm²). Galvanic currents flowing through the couple were determined by measuring voltage drops across the 1 ohm ($\pm 1\%$) resistance with a millivoltmeter or a potentiometer and by applying Ohm's law. Galvanic corrosion rates were calculated from average galvanic currents by applying Faraday's law. Weight losses of coupled and uncoupled metal specimens were determined. Electrode potentials of each uncoupled specimen and of the couple were measured with an L & N type K-2 potentiometer, a saturated calomel electrode, and a saturated potassium chloride bridge. The apparatus was arranged to measure the potential of the whole specimen surface rather than that for a particular point. The potentials are good to ± 0.010 v and are on the saturated calomel electrode scale. Experiments with natural aeration of solution were carried out

in loosely covered vessels, with the use of essentially the same experimental method described above. The volumes of solution used in these experiments were either 750 ml or 2500 ml, depending on rate of acid consumption.

The second type of galvanic couple experiment was a simple weight loss test carried out with two metal specimens maintained in face-to-face contact either by means of a small rubber band at each end or by a rivet. Specimens were 0.13 cm thick, 0.64 cm wide, and 7.6 cm long (area, 0.12 dm²) and were arranged in such a manner that each member of the couple extended 1.3 cm beyond the other at one end. The volume of solution used was approximately 500 ml, and two replicates were placed in each bottle. Chemical corrosion rates for the various metals were based upon tests in which two pieces of the same metal were fastened together as described above. Total specimen areas were always used in converting weight losses to corrosion rates in mils per year. Corrosion rates, summarized under "Increase caused by contact," were obtained by subtracting values for chemical corrosion (single metal) from the value for total corrosion (bimetallic). Chemical corrosion rates are not included in the tables for the sake of brevity.

SINGLE ELECTRODE POTENTIALS

A summary of the electrode potentials of titanium, zirconium, aluminum, and stainless steel in sulfuric acid solutions appears in Table II. These values are for single (uncoupled) specimens after immersion for approximately 15 days in vessels containing couples. Electrode potentials were almost constant after 15 days' immersion with the exception of those for stainless steel in 2*N* acid in the presence of air and those for zirconium in 2*N* acid with all types of aeration. The electrode potentials of titanium varied with immersion time, generally becoming more cathodic (electropositive) with time in the presence of air and more anodic (electronegative) in the absence of air. At any acid concentration, the steady-state values were always most cathodic

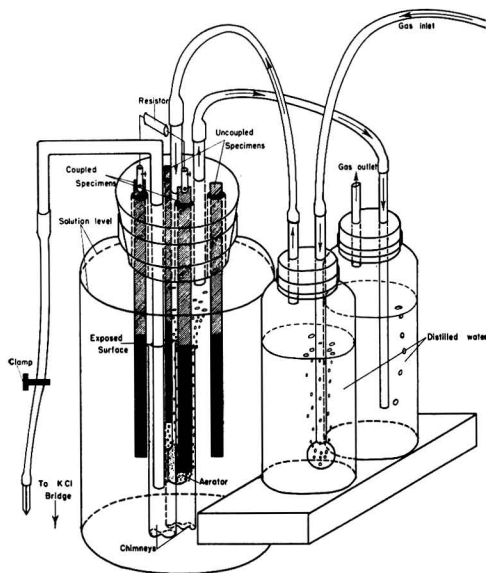


Fig. 1. Apparatus used in open couple experiments

TABLE II. *Single electrode potentials of metals in sulfuric acid solutions, 35°C*

Metal	Electrode potential, volts (referred to saturated calomel electrode)		
	Flow of air	Natural aeration	Flow of helium
0.025N H ₂ SO ₄			
Titanium.....		0.26	-0.55
Zirconium.....			-0.23
Aluminum 2 S-O		-0.54	-0.66
0.10N H ₂ SO ₄			
Titanium ^b	0.19	0.10	-0.70
Zirconium.....	0.31	0.24	-0.28
Aluminum 2 S-O ^a	-0.43	-0.57	-0.64
Stainless steel, type 302.....		0.21	-0.41
1.0N H ₂ SO ₄			
Titanium ^b	0.04	-0.56	-0.67
Zirconium.....	0.09	0.26	-0.33
Aluminum 2 S-O.....	-0.47	-0.43	-0.65
Stainless steel, type 302.....	-0.12-0.20	0.23	-0.35
2.0N H ₂ SO ₄			
Titanium ^c	-0.57-0.07	-0.61	-0.67
Zirconium.....	-0.20-0.05	-0.14-0.05	-0.15-0.25
Stainless steel, type 302.....	-0.14-0.30	-0.14-0.27	-0.35

^a Values for aluminum alloys 24 S-O, 61 S T6, and 3 S H14 varied less than 0.1 v from these values.

^b These values were taken from experiments with aluminum alloy 2 S-O. More positive values were sometimes obtained in experiments with stainless steel, such as: 0.18 v in 0.1N H₂SO₄ with flow of helium, 0.40 v in 1.0N H₂SO₄ with flow of air, and 0.07 v in 1.0N H₂SO₄ with natural aeration.

^c These values were taken from experiments with stainless steel. Electrode potentials were always electronegative during the first 8 or 9 days of immersion in 2N H₂SO₄ with a flow of air but sometimes became more positive later in the experiment.

with a flow of air, most anodic in the absence of air (flow of helium), and intermediate with a limited supply of air (natural aeration). In the absence of air, acid concentration had little effect on the electrode potentials of titanium, but with air present the values became more anodic with increasing concentration. Electrode potential values for titanium obtained during experiments with stainless steel in the presence of air were sometimes more cathodic than those obtained in experiments with commercially pure aluminum because of the passivating effect of the ferric ions. However, ions formed from the alloying elements present in the various aluminum alloys did not appear to affect

the potential of titanium. The electrode potentials of zirconium usually became more noble with time, but there were no significant changes in the potentials of aluminum or stainless steel with immersion time. Electrode potential values for the two grades of zirconium were essentially the same. Potentials of aluminum and stainless steel did not vary greatly with changes in acid concentration, but these metals were more noble in the presence of air. Ranges of electrode potential values are given in Table II for titanium, zirconium, and stainless steel in those solutions in which the measurements were erratic. Electrode potentials of aluminum alloys 24 S-O, 61 S T6, and 3 S H14 varied only slightly from those of commercially pure aluminum (2 S-O). Hence, electrode potential data for 2 S-O in Table II may be used in interpreting corrosion data for the other aluminum alloys.

COUPLES WITH ALUMINUM ALLOYS

Corrosion data obtained in titanium-aluminum alloy open-type couple experiments are summarized in Tables III and IV. The direction of the galvanic currents shows that aluminum alloys are the anodic (electronegative or corroding) members of titanium-aluminum alloy couples immersed in 0.1N sulfuric acid either with a flow of air or with natural aeration. In the absence of air, aluminum alloys are anodic only during the first 2½-9 days of the experiment. Then the galvanic current begins to flow in the opposite direction, indicating that titanium is anodic. Available data show that these reversals in the direction of the galvanic currents occur more readily in higher acid concentrations. In 0.025N sulfuric acid, for example, commercially pure aluminum (2 S-O) was anodic with respect to titanium throughout the experiment even in the complete absence of air, while a reversal in the direction of current flow took place in 1N acid with natural aeration. Relative positions of the time-potential curves for uncoupled specimens of titanium and aluminum alloys are consistent with the direction of the galvanic currents in these experiments (Fig. 2 and 3). A shift in the relative positions of the time-potential curves occurs with reversals in the direction of the currents. Only sample curves are included, but the steady-state electrode potential values in Table II show this consistency. The size of the galvanic current generated in titanium-aluminum couples apparently is not affected by acid concentration but is affected by type of aeration, being smallest with a flow of helium and largest with a flow of air. This may be attributed to the greater potential differences between the two metals in presence of air and perhaps also to the de-

TABLE III. Corrosion of titanium-aluminum alloy open couples in 0.1N sulfuric acid solutions, 35°C, 15 days

Aluminum alloy	Anodic metal	Galvanic corrosion, mpy ^d (calculated from current)	Corrosion rate, mpy (based on weight loss)			
			Titanium		Aluminum alloy	
			Coupled	Un-coupled	Coupled	Un-coupled
Flow of air						
2 S-O ^a	Al	23.5	0.8	0.1	47.3	43.0
24 S-O	Al	40.5	0.4	0.2	102.0	85.1
61 S T6	Al	29.0	1.3	0.0	71.7	59.5
3 S H14	Al	36.5	0.8	0.0	58.5	49.9
Natural aeration ^b						
2 S-O	Al	12.5	4.7	0.0	30.7	26.9
24 S-O	Al	9.0	5.1	0.0	74.9	72.0
61 S T6	Al	12.0	6.3	0.0	50.7	47.8
3 S H14	Al	14.0	6.3	0.0	37.4	33.2
Flow of helium ^c						
2 S-O	Al, Ti	4.0, 1.5	5.4	4.9	29.4	30.6
24 S-O	Al, Ti	0.5, 2.5	3.8	3.8	54.5	54.5
61 S T6 ^b	Al, Ti	4.0, 2.5	5.5	3.2	45.0	44.5
3 S H14 ^b	Al, Ti	5.0, 1.5	4.5	4.8	34.1	29.4

^a Number of replicates 4.^b Number of replicates 2.^c Aluminum alloy was anodic during first 2½ to 9 days of experiment, titanium was anodic remainder of time.^d Equivalent weights used in calculating galvanic corrosion from galvanic current:

Ti	15.97
Al 2 S-O	8.99
24 S-O	10.16
61 S T6	9.06
3 S H14	9.20

polarizing action of air on the cathodic areas of the couple.

Weight loss corrosion data for single (uncoupled) specimens of titanium are consistent with published data (6). Rates for single specimens of titanium indicate that the presence of air inhibits the initiation of chemical corrosion, presumably because of the formation of oxides or layers of adsorbed oxygen. Once corrosion starts, however, air appears to increase the rate, probably because of improved depolarization. Chemical corrosion of aluminum alloys was somewhat more rapid in the presence of air and in higher acid concentrations. Alloys of aluminum studied in this investigation all show the same general behavior in couples with titanium, although individual corrosion rates and electrode potentials do show variations. For both titanium and aluminum alloys, the sum of the corrosion rate of the uncoupled specimen and the galvanic corrosion rate of the coupled specimen is usually greater than the total corrosion rate of the coupled

specimen as determined by weight loss measurements. This tendency toward a negative difference effect is much less pronounced for titanium than for aluminum. Both titanium and aluminum specimens corroded uniformly in these experiments. Multicolored interference films were sometimes formed on titanium surfaces when no weight losses of titanium specimens were observed. Copper and possibly other constituents of the aluminum alloys frequently appeared on the immersed surfaces of the specimens in the form of loosely adhering, spongy deposits. Corrosion rates and electrode potentials of titanium in experiments with those aluminum alloys containing considerable amounts of copper (24 S-O and 61 S T6) were not appreciably different from those obtained with other aluminum alloys. Apparently, the continuous reduction of copper ions to metallic copper on the electronegative surfaces of the aluminum alloys and the titanium-aluminum alloy couples kept the concentration of copper ions below the level required for the passivation of titanium.

Titanium specimens lost weight and acquired the "corroded" appearance in certain environments as a result of coupling with aluminum alloys, in spite of the fact that the direction of the current flow through the couples and the pertinent electrode potential

TABLE IV. Effect of sulfuric acid concentration on corrosion of titanium-aluminum (2 S-O) open couples, 35°C, 15 days

Normality	Anodic metal	Galvanic corrosion, mpy (calculated from current)	Corrosion rate, mpy (based on weight loss)			
			Titanium		Aluminum	
			Coupled	Un-coupled	Coupled	Un-coupled
Flow of air						
0.1 ^a	Al	23.5	0.8	0.1	47.3	43.0
1.0 ^b	Al	8.5	25.6	0.1	69.2	62.6
Natural aeration ^b						
0.025 ^c	Al	10.0	0.0	0.0	25.9	19.1
0.1	Al	12.5	4.7	0.0	30.7	26.9
1.0 ^d	Al, Ti	16.5, 16.0	35.4	26.4	71.0	67.7
Flow of helium						
0.025	Al	3.5	1.7	0.2	21.3	21.6
0.1 ^e	Al, Ti	1.5, 4.0	5.4	4.9	29.4	30.6
1.0 ^f	Al, Ti	5.0, 3.5	14.3	13.6	35.7	36.4

^a Number of replicates 4.^b Number of replicates 2.^c Experiment was 7 days long.^d Aluminum was anodic during first 2 days of experiment, titanium was anodic remainder of time.^e Aluminum was anodic during first 4½ days of experiment, titanium was anodic remainder of time.^f Experiment was 19 days long. Aluminum was anodic during first 7 days of experiment, titanium was anodic remainder of time.

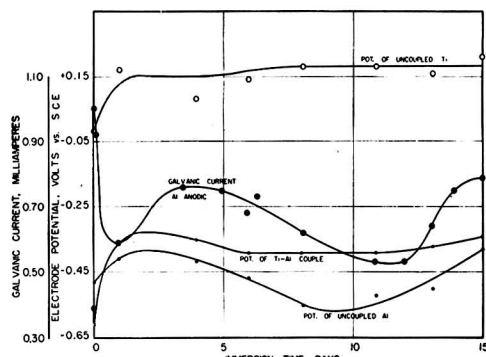


Fig. 2. Titanium-aluminum (2S-O) couple in 0.1N sulfuric acid with flow of air.

values show that titanium was cathodic with respect to aluminum alloys. This type of attack was rapid in 1N sulfuric acid with flow of air and much less so in 0.1N acid with flow of air. It also occurred in 0.1N acid with natural aeration and in 0.025N acid with a flow of helium. Single specimens of titanium were inert in all of these solutions. It is believed that the flow of current through the titanium-aluminum couples results in evolution of active hydrogen on titanium surfaces which, in turn, destroys the oxide film that ordinarily protects titanium in these solutions. Mears and Brown (7) explained the corrosion of stainless steel as a result of contact with aluminum in 0.5% sulfuric acid in the same manner. The term "cathodic corrosion" has been applied to this phenomenon (8). In the case of titanium, a greater supply of air decreases the tendency for this reaction to occur because the protective film is repaired more readily. Higher acid concentrations aid in the destruction of the protective film and hence promote the reaction. The effectiveness of active hydrogen in destroying passivity was demonstrated by electrolyzing sulfuric

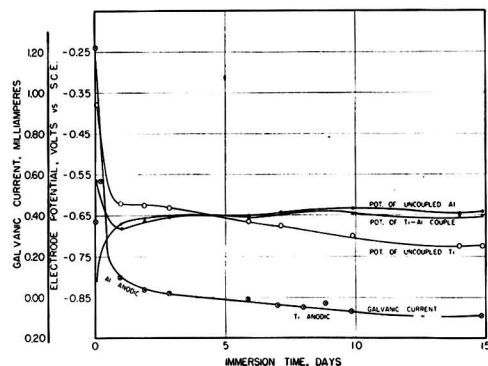


Fig. 3. Titanium-aluminum (2S-O) couple in 0.1N sulfuric acid with flow of helium.

TABLE V. Corrosion of titanium-aluminum alloy face-to-face contact couples in 0.1N sulfuric acid solutions, 35°C, 15 days

Aluminum alloy	Corrosion rate, mpy			
	Total corrosion		Increase caused by contact	
	Ti ^a	Al	Ti ^a	Al
Flow of air				
2 S-O ^b	1.1 ^c	38.2	1.1	9.5
3 S H14	3.9	38.1	3.9	1.8
Natural aeration				
2 S-O ^b	4.9 ^c	28.5	4.9	1.6
24 S-O	2.7	62.7	2.7	2.1
61 S T6	4.4	42.9	4.4	2.0
3 S H14 ^b	4.2	31.3	4.2	2.5
Flow of helium				
2 S-O	3.9 ^c	23.9	-1.2	0.8
24 S-O	3.6	58.3	-1.5	8.9
3 S H14	3.0	25.9	-2.1	-2.8

^a To correct for uncorroded areas multiply corrosion rates obtained with flow of air and natural aeration by 1.25; with flow of helium by 1.10.

^b Number of replicates 4.

^c Values obtained in experiments in which a rivet replaced the rubber bands are as follows: flow of air (2 replicates) Ti 2.8, Al 36.2; natural aeration (5 replicates) 5.3, 29.0; flow of helium (2 replicates) 4.8, 28.0.

acid solutions using a platinum anode and a titanium cathode with a cathode current density of 4 ma/dm². In 1N sulfuric acid with a flow of air the titanium cathode corroded at the rate of 27.4 mpy during a 5-day test while another titanium specimen immersed in the same solution without an external current lost weight at the rate of only 0.5 mpy. Corresponding values for 0.1N acid with natural aeration were 4.9 and 0.0 mpy.

Table V shows that titanium corrodes at moderate rates as a result of face-to-face contact with aluminum alloys in 0.1N sulfuric acid in the presence of air, although two pieces of titanium in contact under the same conditions are inert. For all conditions of aeration, "total corrosion" rates for titanium and aluminum alloys in face-to-face contact are in general agreement with corrosion rates for "coupled" specimens in open type couples (Table III). This is also true for "increase caused by contact" and the difference in corrosion rates between "coupled" and "uncoupled" specimens. Corrosion of titanium specimens appeared to be uniform except for some uncorroded areas on the contact sides which were not "wetted." These uncorroded areas averaged about 20% of the total specimen area in the presence of air and 10% in the absence of air. Corrosion rates in Table V are based upon total specimen area,

TABLE VI. Corrosion of zirconium^a-aluminum alloy open couples in 0.1N sulfuric acid solutions, 35°C, 15 days

Aluminum alloy	Anodic metal	Galvanic corrosion, ^d mpy (calculated from current)	Corrosion rate, mpy (based on weight loss)			
			Zirconium		Aluminum	
			Coupled	Un-coupled	Coupled	Un-coupled
Flow of air						
2 S-O	Al	12.5	0.08	0.0	44.2	42.3
24 S-O	Al	22.5	0.1	0.0	82.9	78.0
61 S T6	Al	11.5	0.1	0.04	68.0	60.1
3 S H14	Al	17.5	0.1	0.0	50.8	47.0
Natural aeration ^b						
2 S-O ^c	Al	9.0	0.1	0.04	32.2	26.8
61 S T6	Al	10.5	0.07	0.02	39.3	38.1
Flow of helium						
2 S-O	Al	2.5	0.04	0.03	34.4	32.0
24 S-O	Al	1.0	0.07	0.03	60.6	59.1
61 S T6	Al	2.0	0.04	0.0	54.4	50.9
3 S H14	Al	2.5	0.1	0.0	30.8	33.6

^a Low purity zirconium.

^b Number of replicates 2.

^c Experiment was 11 days long.

^d Equivalent weight used in calculating galvanic corrosion from galvanic current: Zr 30.41.

but estimated correction factors appear in a footnote. Aluminum specimens appeared uniformly corroded at the end of the test period and were covered with loosely adhering red or dark deposits. Substitution of an aluminum rivet for the rubber bands did not substantially change the corrosion rates (Table V, footnote c).

Table VI includes corrosion data for zirconium (low purity), aluminum alloys, and zirconium-aluminum alloy open-type couples in 0.1N sulfuric acid solutions. Both the direction of flow of the galvanic currents and the electrode potentials of uncoupled specimens of the metals (Table II) show that the aluminum alloys are always the anodic or corroding members of the couple. Galvanic corrosion of aluminum alloys was always appreciable and was much greater in the presence of air. Corrosion rates for aluminum alloys and the negative difference effect of aluminum in the presence of air are in agreement with the data for titanium-aluminum alloy couples. Weight losses for zirconium specimens, single or coupled with aluminum alloys, were negligible in these solutions. However, the surfaces of zirconium specimens in contact with aluminum alloys frequently became dull or blistered, and x-ray determinations show high concentrations of zirconium hydride on these surfaces. In another series of experiments, contact with aluminum alloys in 1 and 2N acid solutions caused zirconium to

undergo slight weight losses (equivalent to 0.3 mpy) and pronounced hydride formation. Uncoupled specimens of zirconium were inert in these solutions and remained unchanged in both appearance and weight. Zirconium of high purity in contact with commercially pure aluminum did not lose weight or change in appearance. Data for zirconium and aluminum in face-to-face contact experiments are in general agreement with these results.

COUPLES WITH STAINLESS STEEL

The curves in Fig. 4 represent a typical open-type couple experiment with titanium and type 302 stainless steel in 2N sulfuric acid with a flow of helium. The electrode potential of the coupled titanium specimen (and of the couple) became the same as that of the single stainless steel specimen soon after coupling, showing that titanium is readily polarized in this environment. When the couple was disconnected, the "coupled" titanium specimen quickly acquired the same electrode potential as the single specimen (within 0.02 v in 3 to 7 min). The specimen was polarized again within ½ min after reconnecting the couple. Time-potential curves for the uncoupled stainless steel specimen and for the couple in 2N sulfuric acid with a flow of air are somewhat farther apart and more erratic than the curves in Fig. 4. In the presence of air the titanium specimen was polarized as described above but was not readily depolarized. In this environment the "coupled" specimen was still noble a day or more after breaking the couple.

Data for titanium-stainless steel open-type couples summarized in Table VII show that galvanic currents in sulfuric acid solutions were small or negligible in size in spite of the large differences between the electrode potentials of the two metals

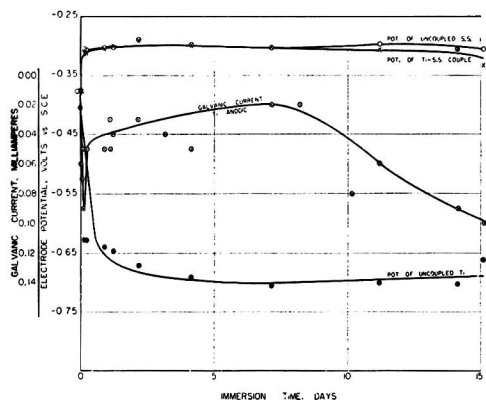


FIG. 4. Titanium-stainless steel couple in 2N sulfuric acid with flow of helium.

TABLE VII. Corrosion of titanium-stainless steel (type 302) open couples in sulfuric acid solutions, 35°C, 15 days

Normality	Anodic metal	Galvanic corrosion, ^g mpy (calculated from current)	Corrosion rate, mpy (based on weight loss)			
			Titanium		Stainless steel	
			Coupled	Un-coupled	Coupled	Un-coupled
Flow of air						
1.0	S.S. ^d	1.5	0.7	0.2		
2.0 ^a	Ti	0.5	0.2	40.8	4.1 ^e	0.1
Natural aeration						
0.1 ^b	Ti	0.0	0.0	0.0	0.0	0.0
1.0 ^c	Ti	0.0	0.1	22.2	0.2	0.1
2.0 ^b	Ti	0.0	0.2	43.1 ^f	1.0 ^f	0.6
Flow of helium						
0.1 ^{a, g}	Ti ^h	0.0	0.05	1.7	2.1	3.1
1.0	Ti	0.5	1.3	13.7	11.2	13.4
2.0 ^{a, g}	Ti	3.0	4.5	19.8	24.1	23.9

^a Number of replicates 3.^b Number of replicates 4.^c Number of replicates 2.^d Corrosion rates for stainless steel were 3 to 5 mpy but most of corrosion occurred above the stopper because of a leak. No galvanic corrosion was detected before the second day or after the twelfth day.^e Values were 10.7, 1.6, 0.2 mpy.^f Rate for titanium is made up of 3 values, the fourth, 10.4 mpy, was omitted. Rate for stainless steel is made up of 3 values, the fourth, 9.2 mpy, was omitted.^g Lengths of experiments varied from 13.9 to 19.0 days.^h Titanium was cathodic in one of these experiments.ⁱ Equivalent weight used in calculating galvanic corrosion from galvanic current: stainless steel 26.14.

(Table II, Fig. 4). The direction of the current flow indicated that titanium was anodic with respect to stainless steel in all environments studied except 1*N* sulfuric acid with flow of air. This is in agreement with the electrode potential values in Table II. Weight loss corrosion data for uncoupled specimens of titanium were consistent with data from other sources (6). Coupling with stainless steel in solutions in which titanium normally undergoes chemical corrosion and is less noble than stainless steel causes large decreases in the chemical corrosion rates of titanium. This is evidently caused by anodic polarization of titanium. Since uncoupled specimens of titanium present in the same vessels corroded at the normal rates, this relative inertness of the coupled specimens cannot be ascribed to the presence of the ferric ion. Corrosion of stainless steel in these environments was quite erratic and, apparently, was not affected by contact with titanium.

Corrosion rates obtained for titanium in face-to-face contact with stainless steel are in good agree-

ment with the values for open-type couples (Table VII). For example, the following corrosion rates were obtained for titanium in face-to-face contact with stainless steel in 2*N* sulfuric acid: flow of air 1 mpy, natural aeration 2 mpy, flow of helium 6 mpy.

Zirconium-stainless steel couples generated only small galvanic currents (equivalent to 1 mpy or less) in 2*N* sulfuric acid with the three types of aeration and in 0.1 and 1*N* acid with a flow of helium, even though electrode potential measurements (Table II) generally show zirconium to be less noble than stainless steel. Furthermore, the direction of the tiny currents frequently did not correspond to the relative values of the potentials. Coupled or uncoupled, the low purity zirconium corroded slowly in 2*N* sulfuric acid (up to 0.3 mpy in the absence of air). The high purity zirconium did not show appreciable weight losses. Both zirconium and stainless steel were unaffected by contact with each other. Data obtained in face-to-face contact experiments were in agreement with those for the open-type couples.

CONCLUSIONS

Contact between titanium and aluminum alloys in sulfuric acid solutions (0.025–1*N*) causes galvanic corrosion. The aluminum alloy tends to be the anodic (corroding) member of the couple in lower acid concentrations and in the presence of air. In stronger acid solutions, especially when air is absent or in limited supply, a reversal in the direction of the current flow takes place after a number of days' immersion and titanium becomes anodic. Contact between zirconium and aluminum alloys in these solutions always results in galvanic corrosion of the latter. Zirconium of high purity is inert in these environments. On the other hand, surfaces of low purity zirconium specimens acquire a dull and blistered appearance and a high concentration of zirconium hydride, although weight losses are small. The severity of galvanic attack in these couples increases with air supply at the metal surfaces. The direction of flow of the galvanic current is consistent with the relative values of the electrode potentials of the single metal specimens.

Contact between titanium and stainless steel (type 302) in sulfuric acid solutions (0.1–2*N*) causes little or no galvanic corrosion, although electrode potential measurements show titanium to be much less noble than stainless steel. This is the result of the ease with which titanium undergoes anodic polarization. Little, if any, galvanic corrosion occurred in zirconium-stainless steel couples, although stainless steel was generally anodic according to electrode potential measurements.

Corrosion rates obtained for uncoupled titanium specimens are in good agreement with published data for chemical corrosion of titanium. However, contact with other metals sometimes produced important changes in the chemical corrosion properties of titanium. Contact with aluminum alloys in certain solutions in which titanium is ordinarily inert and cathodic (noble) with respect to the aluminum alloys causes titanium to corrode. This is believed to be the result of the destruction of the protective oxide film by the active hydrogen evolved at the cathode surfaces. Contact with stainless steel in solutions in which titanium is anodic decreases the chemical corrosion rates of titanium because of anodic polarization of titanium surfaces.

The results of experiments in which metals were merely in electrical contact are in substantial agreement with those of experiments in which the metal

specimens were maintained in actual face-to-face contact with rubber bands or rivets.

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

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Electrodeposition of Cellulose¹

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ABSTRACT

Cellulose has been plated at the anode from solutions containing approximately 1% cellulose, where the solvent is an alkaline sodium zincate modified by additions of urea.

INTRODUCTION

Some time ago the senior author (1) investigated cellulose solubility in alkaline solutions and found that the solvency power of sodium zincate solutions is markedly improved by the addition of specific amounts of urea or related materials. Sodium zincate solutions alone have a restricted field of application, exhibiting solvency power for only a limited number of cellulose materials and being ineffective for others. This is true below 5°C, which is the required maximum temperature at which sodium zincate exerts solvency power on cellulose. As the cellulosic content of sodium zincate solutions increases, viscosities become enormous. Some relief may be achieved by the use of excessive amounts of sodium zincate, but this introduces other difficulties.

In the case of the sodium zincate-urea solvents, it is particularly noticeable that an increased number and variety of forms of regenerated cellulose may be treated. These embrace a wide variety of paper mill and factory wastes which can be put in solution at room temperatures or above without the necessity of cooling or exact temperature control.

The basic thought which led to this investigation was that mill scraps and other factory wastes could be dissolved and then electroplated to a useful form. There is a possibility of electroplating on wire to form an insulating cover, or plating on wire screen to form a protective coating, or simply to make a fine grade paper. Upon careful consideration, many more applications could be found.

The solvent is commonly prepared by mixing together either an alkaline aqueous solution of sodium zincate and urea or by the addition of urea and zinc oxide to an aqueous solution of sodium or potassium hydroxide. It is interesting to note that composition ranges are reasonably limited. Urea is effective at about 4 to 10% by weight of solution,

and preferably from 6 to 10%. Below this range the solvency power of the solution is decreased, while little worth-while improvement results at urea concentrations above 10%. The zinc oxide percentages may vary from a minimum of 2 to the saturation value, while the NaOH varies from 7 to 15%. Solvency power is adversely affected by concentrations of zinc oxide and caustic below the minimum, while above the maximum little advantage is gained and some difficulties might be experienced. A typical effective solvent is one composed of 4.5% zinc oxide, 10% caustic, 10% urea, and the balance water. Chemicals such as cyanamid, guanidine, and guanylurea, for example, which hydrolyze with alkalies or zincates to form urea, may be employed in amounts equivalent to the urea.

It appears that amphoteric metals forming hydroxides and salts or ammonia complexes might be employed in place of zinc oxide. Experimental work over a wide range with copper, nickel, and cobalt oxides and hydroxides showed that their solubility in caustic and urea combinations was low and compounds were not formed which showed cellulose solvency at room temperatures. In the case of the amphoteric metals such as aluminum and tin, aluminates offered little encouragement but stannates with urea gave useful effects. Solutions of 8-15% NaOH and 1-5% sodium stannate were found to dissolve on rayon and related materials at low temperature. A minimum of 10% NaOH was necessary with 2-3 g stannate/100 cc solvent. Clear solutions were obtained up to 5% regenerated cellulose content after a few minutes of constant stirring. However, after approximately 15 min the solution gelled and within an hour was converted to a stiff clear gel. Addition of urea reduced the viscosity to approximately 20% of the viscosity of the solution with no urea.

From solvents such as the above, with control of viscosity, electrodeposition of cellulose was investigated.

EXPERIMENTAL

Solvent preparation.—The solvent was prepared by the addition of urea and zinc oxide to an aqueous solution of sodium hydroxide.

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Solvent

Zinc oxide.....	4.5% by weight
Caustic.....	10% by weight
Urea.....	10% by weight
Water.....	75.5% by weight

Electroplating solution.—A series of cellulose solutions were made as follows:

Electroplating Solution

Concentration of cellulose material (% by weight)	Consistency of bath
0.5	Very thin
1.0	Thin
1.5	Thin
2.0	Gels after standing several hours
2.5	Gels after standing several hours

It is apparent that the 2.0 and 2.5% solutions must be used before they gel. The 1% solution was used for electrodeposition experiments.

The plating bath was contained in glass beakers into which the electrodes were immersed. Each electrode was supported by a copper conductor bar. A selenium rectifier of 75 amp/0–15 v or 150 amp/0–7.5 v was utilized.

Test of electrodes

Electrode material	Current density 0.2 amp/ft ²	Current density 1.0 amp/ft ²
Stainless steel....	—	Zinc deposited at cathode
Zinc plated steel..	—	Zinc deposited at cathode
Tin plate.....	—	Zinc deposited at cathode
Bronze.....	Compound deposited at anode	Zinc deposited at cathode
Copper.....	Compound deposited at anode	Zinc deposited at cathode
Lead.....	Compound deposited at anode	Zinc deposited at cathode

Chemical testing of the film.—In order to prove that the substance plated was cellulose, the plated material was scraped off the electrode and dissolved in concentrated sulfuric acid and diluted in water. This solution was refluxed for several hours to hydrolyze the cellulose to glucose. The refluxed liquid contained a sugar as indicated by Fehling's solution. The dried plated material was also tested for insolubility in hot water and solubility in Schweitzer's reagent (cuprammonium reagent). The results of these tests showed the plated material to be cellulose and it was concluded that cellulose can be plated from a solution of sodium zincate and urea onto a copper, bronze, or lead anode. Copper was arbitrarily chosen as the electrode material for use in the remainder of the experiments.

Electroplating range.—The conditions necessary

for the electrodeposition of cellulose were determined by conducting a series of depositions for 10 min at constant current density. Seven trials at an electrode spacing of one inch were made and the required conditions were found to be:

Electroplating Range

Current range.....	20–120 milliamp
Voltage range.....	1.10–1.28 v
Current density range.....	0.137–1.11 amp/ft ²

Above the upper limit of current density, zinc was plated at the cathode. With a considerable increase in current density (80 amp/ft²) spongy zinc deposited at the cathode and cellulose migrated toward the anode, but did not adhere. It appears that the cellulose was coagulated but not deposited under these conditions.

Estimate of current efficiency.—Cellulose is not a substance possessing molecular homogeneity. Molecules widely varying in weight are present in a solution. It was necessary to deal with averages, such as average molecular weights and average chain lengths. Current efficiencies calculated on the assumption of a molecular weight of 50,000 and a valence change equivalent to 2 are low. Increasing the cellulose concentration improved the efficiency, but this was limited by the point at which the solution gelled. Current efficiency increased as current density decreased.

Current Efficiency

% Cellulose	Current density	Average current efficiency
	amp/ft ²	%
1	0.320	3.30
	0.513	2.38
	0.641	1.99
2	0.575	2.98

Results.—When the anode was sufficiently covered to insulate it, the deposition of cellulose ceased. Several platings could be made from the same bath.

An attempt was made to increase the amount of material deposited and improve the film characteristics. This was done by doubling the cathode area and keeping the same anode area; thus, the anode current density was doubled and the cathode current density remained the same. The voltage was 1.28 v in both instances but the current increased from 150 to 300 milliamp. The only noticeable effect was a slight increase in material deposited.

In order to strip the cellulose film from the anode, it was necessary to allow the plated cellulose to air dry. The anode was immersed in methyl alcohol to facilitate the drying operation. After drying, the unit was washed with 6N HCl to dissolve any metallic salts or hydroxides transported with the cellulose during the plating operation. Following

this treatment, the film was easily removed and then allowed to dry. The film was like a soft tissue paper and was about 0.006 in. in thickness and quite fragile.

In order to improve the characteristics of the plated material, various plasticizers were incorporated in the baths as additives. The examination was only cursory, since the primary point of interest was the determination of the necessary plating conditions. Among the plasticizers incorporated in the solution were shellac, ammonia casein, glycerine, methyl abietate, all without success. It is believed further experimentation should include glycol derivatives and other compounds such as alkaline soluble resins to impart wet strength to the film.

Platings were also made on wire screen, wire, and on other irregular objects, but the film could not be stripped.

CONCLUSIONS

The electrolyte for a typical plating bath would have the following weight-per cent composition: cellulose, 1.0; zinc oxide, 4.5; sodium hydroxide, 10.0; urea, 10.0; water, 74.5. Typical plating conditions call for an anode current density of 0.137–1.11 amp/ft², cell voltage, 1.10–1.28 v, average current efficiency, 1.99–3.30 %, average deposition rate, 3.30–5.46 g/amp-min.

A suitable solution contains 1–2.5 % by weight of cellulose and, when plating, the current density must be closely controlled to prevent the deposition of zinc at the cathode.

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

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The Electrolytic Reduction of Isobutyraldehyde in Acid Solution¹

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ABSTRACT

The electrolytic reduction of isobutyraldehyde has been carried out at cathodes of cadmium, zinc, mercury, and lead. The influence of the physical condition of the cathode has been studied. Preparation of the surface has been shown to have a marked effect on the products obtained at lead and zinc.

INTRODUCTION

This study was undertaken to show the influence of the cathode material on the electrolytic reduction of an aliphatic aldehyde having a branched chain adjacent to the carbonyl group. It has been previously shown that straight chain aliphatic aldehydes are reduced to the primary alcohol as main product at cathodes of cadmium, mercury, and lead (1-3). The yield of hydrocarbon was found to increase with temperature (1). The only simple branched chain aldehyde which has been reduced is isobutyraldehyde. Hibbert and Read (2) found that it behaved similarly to the straight chain aldehydes in being reduced to isobutyl alcohol as the main product at a lead cathode. Since its behavior at other cathodes had not been studied, isobutyraldehyde was chosen for the present investigation.

APPARATUS AND PROCEDURE

The apparatus and general procedure was the same as that described in previous communications (4-6). Only cathodes of zinc, cadmium, mercury, and lead were used in this investigation because they had been shown to be the most active in the reduction of aliphatic carbonyl compounds (3).

Pure isobutyraldehyde (bp 63°C) was obtained from a crude starting material by fractionation in a high precision column.

RECOVERY OF PRODUCTS

Isobutane and isobutene.—In the first experiments the calcium chloride tube originally used (3) was replaced by a U-tube cooled in an ice salt bath to remove the isobutyraldehyde carried over in the gas stream. A very small amount of aldehyde was

found in the dry ice-isopropyl alcohol trap along with the hydrocarbons. In later experiments a tube containing an alkaline solution of hydroxylamine hydrochloride was inserted in the train before the ice-salt trap and a calcium chloride tube before the dry ice-isopropyl alcohol trap. In this way the hydrocarbons were obtained uncontaminated.

At certain cathodes some isobutene was formed along with the isobutane. It was determined in some typical experiments by analysis of the gases formed by allowing the liquid hydrocarbons to vaporize.

Products in the catholyte.—After completion of the runs the catholyte together with the washings of the porous cup and cathode were poured into a distilling flask and the isobutyl alcohol and unreduced aldehyde removed by distillation. In certain experiments a heavy oil, which turned out to be paraisobutyraldehyde, was found. This was separated from the diluted catholyte before distillation. The distillate was then fractionated in a high precision column. The efficiency of the separation was determined by fractionating known mixtures of isobutyraldehyde isobutyl alcohol, and water. It was found that over 95% of the aldehyde distilled at 60°-63°C. The temperature then rose rapidly to 88°C at which the constant boiling mixture of isobutyl alcohol and water distilled. It was decided to make the cut at 77°-80°C. There was no loss on account of hold up in the column, as water started to come over immediately after the isobutyl alcohol-water fraction.

The isobutyl alcohol-water fraction was dried with anhydrous potassium carbonate, redistilled, and weighed. Water content was determined by refractive index and found to be very small.

Small quantities of solid paraisobutyraldehyde (MP 59°-60°C) were sometimes found in the tube cooled in the ice salt mixture.

The solid metal cathodes were cast in a cold mold, and at 50°C under their melting points. Besides the usual anodization of zinc and cadmium

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in sulfuric acid and preparation of the lead by the Tafel procedure (7) the metals were etched in nitric acid and lead was anodized in perchloric acid. All of the solid metals were studied in electropolished condition also. The baths for polishing were as follows: ethyl alcohol-phosphoric acid for zinc (8) and cadmium and perchloric acid-acetic anhydride for lead (9). Unless otherwise noted, cathodes of zinc were dipped in dilute nitric acid, those of cadmium anodized in sulfuric acid, and those of lead given a "Tafel" preparation.

Only 5 g of isobutyraldehyde per 100 cc of catholyte was used in each run on account of its low solubility. The use of a blending agent was undesirable on account of the difficulties it might cause in separating the products. In the recovery of products from runs with all cathodes except mercury, four runs were combined. In some of the experiments two cells were connected in series.

DISCUSSION OF RESULTS

The effect of experimental conditions on the electrolytic reduction of isobutyraldehyde is shown in the following tables and discussion.

It may be seen in Table I that the temperature of the catholyte has a marked effect not only on the total yield but also on the type of product. At the lower temperature the zinc cathode was practically inactive, while the yields of alcohol were much higher with yields of hydrocarbon correspondingly lower at cathodes of cadmium and lead. The behavior of mercury was exceptional. No hydrocarbon was found under any conditions. There were found considerable amounts of a heavy oil, which turned out to be paraisobutyraldehyde. As in the case of cadmium and lead the lower temperature was favorable to the formation of the alcohol.

Effect of acid concentration.—It was found that lowering the acid concentration in the catholyte from 30 to 10% had little effect on the yield of hydrocarbon at any cathode. The yields of alcohol, however, were about 10–15% higher than those shown in Table I at temperatures of 58°–61°. Considerable amounts of paraisobutyraldehyde were found in the catholyte of 10% sulfuric acid with the mercury cathode.

Effect of current density.—Lowering the current density from 0.05 amp/cm² to 0.02 amp/cm² had no beneficial effect. In fact, some of the yields were decreased.

Effect of physical structure of cathode.—Several interesting points are illustrated in Table II. In the first place, zinc cathodes are much more active after being treated with nitric acid than after the usual anodization. The higher yields of alcohol obtained at the same type of cathode were due to

TABLE I. Influence of temperature

Anode: lead cylinder; anolyte: 10% sulfuric acid; catholyte: 100 cc of 30% sulfuric acid with 5 g of isobutyraldehyde; cathode area: 100 cm²; amp: 5; current density: 0.05 amp/cm²; duration of run: 1½ hr (theoretical for reduction of isobutyraldehyde to isobutane).

Products of four runs combined

Cathode material	Temp, °C	Grams of isobutane	% yield of isobutane	Grams of isobutyl alcohol	% yield of isobutyl alcohol
Zinc, 370	58-61	3.6	23.0	2.8	13.7
Same	58-61	3.6	23.0	3.2	15.1
Same	58-60	3.4	21.1	3.5	17.0
Same	18-21	0.1	0.6	1.4	6.8
Same	18-21	0.1	0.6	1.1	5.3
Cadmium, 270	58-60	4.9	30.4	3.9	19.0
Same	58-60	4.7	29.1	3.8	18.5
Same	58-60	5.2	32.3	4.4	21.2
Same	59-61	5.3	32.9	4.5	21.8
Same	19-22	3.1	19.3	6.6	32.1
Same	18-21	3.3	20.5	7.2	35.0
Mercury*	58-61	0	0	1.5	7.2
Same*	58-61	0	0	1.9	9.6
Same*	18-21	0	0	10.2	49.6
Same*	18-21	0	0	12.1	59.0
Same	19-21	0	0	12.4	60.1
Lead, RT	58-61	3.8	23.5	5.8	28.3
Same	58-60	4.0	24.8	6.4	31.1
Same	58-61	4.0	24.8	6.2	30.2
Same	19-21	1.6	10.0	9.0	43.6
Same	18-21	1.5	9.3	8.7	42.3

* Catholyte: 20 g of isobutyraldehyde in 400 cc of 30% sulfuric acid; duration of run: 6 hr. Numbers following the names of the cathodes are the mold temperatures of the cast. RT signifies room temperature.

longer treatments with nitric acid. Treating a machined cadmium surface similarly raised the yield of alcohol, but had no effect on that of the hydrocarbon. The effect on a lead cathode was to increase the amount of hydrocarbon at the expense of the alcohol.

The effect of electropolishing on zinc was to make it less active for hydrocarbon and alcohol formation. The activities of cathodes of cadmium and lead were practically unchanged.

The temperature at which the electrodes were cast was an important factor with zinc and cadmium but not with lead. Higher yields of the alcohol were obtained at cathodes cast at the lower temperature.

It is possible that differences in behavior of the two types of cathodes may be due to crystal orientation. The orientation in the metal cast at room temperature would be random with small grain size, while preferred orientation would be increased by the formation of large columnar crystals resulting from casting the metal 50°C under its melting point. Similarly, the effects of etching with nitric acid could be ascribed to an increase in preferred orientation.

TABLE II. *Effect of physical structure of cathode*
Temp, 52°-61°. All other conditions as in Table I.

Cathode material	Grams of isobutane	% yield of isobutane	Grams of isobutyl alcohol	% yield of isobutyl alcohol	Treatment of cathode
Zinc, RT, 2 sets	2.8	17.5	4.8	23.3	Dil. HNO ₃
	3.5	21.7	5.8	28.2	Dil. HNO ₃
Zinc, RT, set 1	2.1	13.0	1.7	8.5	Anod. H ₂ SO ₄
	1.2	7.5	1.3	6.3	Anod. H ₂ SO ₄
Same	3.7	23.0	6.9	33.0	Dil. HNO ₃
Same	3.7	23.0	6.1	30.0	Dil. HNO ₃
Zinc, RT, set 2	0.8	5.0	1.0	5.0	Anod. H ₂ SO ₄
	0.6	3.6	1.3	6.3	Anod. H ₂ SO ₄
Same	3.7	23.0	6.9	33.5	Dil. HNO ₃
Same	3.6	22.5	6.7	32.5	Dil. HNO ₃
Same	2.5	15.4	1.0	5	Pol., electropol.
Same	2.2	13.6	1.1	5.5	Pol., electropol.
Zinc, 370, 2 sets	3.6	23.0	2.8	13.7	Dil. HNO ₃
	3.6	23.0	3.2	15.1	Dil. HNO ₃
	3.4	21.1	3.5	17.0	Dil. HNO ₃
Zinc, 370, set 1	3.4	21.0	5.8	28.0	Dil. HNO ₃
	2.2	13.6	5.3	25.5	Dil. HNO ₃
Same	2.4	15.0	4.5	22	Anod. H ₂ SO ₄
Same	5.0	31	6.2	30.5	Dil. HNO ₃ , each run
Zinc, 370, set 2	2.3	14.2	5.3	25.5	Dil. HNO ₃
	3.0	18.7	5.3	25.5	Anod. H ₂ SO ₄
Cadmium, RT, set 1	5.3	32.8	6.0	29.0	Anod. H ₂ SO ₄
	5.2	32.1	6.4	31.0	Anod. H ₂ SO ₄
Cadmium, RT, set 2	5.0	31.0	6.5	32.0	Anod. H ₂ SO ₄
	5.3	32.8	5.8	28.0	Anod. H ₂ SO ₄
Cadmium, 270, set 1	5.8	36	5.3	26	Anod. H ₂ SO ₄
	3.9	24	5.3	26	Anod. H ₂ SO ₄
Cadmium, 270, 2 sets	4.9	30.4	3.9	19	Anod. H ₂ SO ₄
	4.7	29.1	3.8	18.5	Anod. H ₂ SO ₄
Same	5.2	32.3	4.4	21.2	Anod. H ₂ SO ₄
Same	5.3	32.8	4.5	21.8	Anod. H ₂ SO ₄
Cadmium, 270, mach. 2 sets	5.5	34.2	4.0	19.5	Anod. H ₂ SO ₄
	5.2	32.3	3.8	18.5	Anod. H ₂ SO ₄
	5.2	32.3	3.8	18.5	Anod. H ₂ SO ₄
	5.2	32.3	4.2	20.4	Anod. H ₂ SO ₄
Cadmium, 270, mach. set 1	5.7	35.5	4.7	23.0	Pol. electropol.
	5.9	36.5	5.5	26.5	Pol. electropol.
	5.1	31.5	6.2	30.5	1:1 HNO ₃
	5.3	32.7	6.1	29.5	1:1 HNO ₃
Lead, RT, 2 sets	3.8	23.5	5.8	28.3	Tafel prep.
	4.0	24.8	6.4	31.1	Tafel prep.
	4.0	24.8	6.2	30.2	Tafel prep.
Lead, RT, set 1	4.3	26.5			Tafel prep.
	3.9	24.0			Tafel prep.
	2.9	18.0	5.1	25	Tafel prep.

TABLE II—Continued

Cathode material	Grams of isobutane	% yield of isobutane	Grams of isobutyl alcohol	% yield of isobutyl alcohol	Treatment of cathode
Same	2.4	14.6	6.5	31.5	Tafel prep., 2 C.D.
Same	2.9	18.0	5.4	26.5	Anod. HClO ₄
Same	3.0	18.5	5.3	26.0	Anod. HClO ₄ , Tafel prep.
Same	3.3	20.5	4.8	23.5	1:1 HNO ₃ , Tafel prep.
Lead, RT, set 2	3.4	21.5	5.2	25.5	Tafel prep.
	4.8	29.5	5.0	24.5	Tafel prep.
Same	3.6	22.3	6.3	30.0	Tafel prep.
	3.9	24.0	6.0	29.0	Tafel prep.
Same	3.8	23.5	6.5	32.0	Tafel prep.
Lead, Rt, set 3	3.4	21.0	5.7	28.0	Tafel prep.
	2.8	17.2	6.7	33.0	Tafel prep.
	6.2	38.0	4.1	20.0	3 hr, 1:1 HNO ₃
Same	6.4	40.0	5.3	26.0	1½ hr., 1:1 HNO ₃
Lead, 270, 2 sets	3.8	23.6	5.8	28.2	Tafel prep.
	4.3	26.7	6.1	29.6	Tafel prep.
Same	4.1	25.5	6.4	31.1	Tafel prep.
	4.1	25.5	6.9	33.4	Tafel prep.
Lead, 207, set 1	2.8	17.2	6.4	31.3	Tafel prep.
	5.8	36.5	5.0	24.5	4 hr, 1:1 HNO ₃
Lead, 270, set 2	4.5	28.0	6.3	30	Tafel prep.
	4.3	27.0	6.3	30	Tafel prep.
Lead, mach.	3.3	20.5	5.7	28	Electropol.
	3.5	21.5	6.0	29	Electropol.
Same	5.0	31.0	6.5	31.5	Electropol., Tafel prep.
Same	3.1	19.0	6.2	30.5	Pol., electropol.
Same	4.0	24.5	5.5	27.0	Tafel prep.

Mach. after cathode: surface smoothed by machining. Two sets: runs from 2 sets of cathodes combined. Dil. HNO₃: dipped in dilute nitric acid. Anod. H₂SO₄: anodized in 20% sulfuric acid. Pol.: polished. Electropol.: electropolished. Tafel prep.: Tafel preparation. Anod. HClO₄: anodized in 20% HClO₄. 2 C.D.: double the usual current density.

After many Tafel preparations the yield of hydrocarbon decreased at one set of lead cathodes cast at room temperature. Small amounts of paraisobutyraldehyde were found as in the case of mercury.

Formation of olefine.—At all cathodes except mercury the isobutane was found to contain small amounts of unsaturated material, presumably, 2-methylpropene. As much as 13% was found from the reduction in the total hydrocarbon at the zinc cathode cast at 370°C.

GENERAL CONCLUSIONS

Isobutyraldehyde has been reduced electrolytically to isobutane, isobutene, and isobutyl alcohol. The highest yield of hydrocarbon, 40%, was obtained at a lead cathode which had been allowed to stand in strong nitric acid for several hours. The highest yield of the alcohol, 60.1%, was obtained at a mercury cathode. No hydrocarbon at all was found at the mercury cathode.

Decreasing the temperature of the catholyte caused a lowering of the activity of cathodes of zinc and an increase in the yield of the alcohol at cathodes of cadmium, mercury, and lead.

In all cases, decreasing the acid concentration led to an increase in the yield of the alcohol and hence to an over-all increased conversion of the aldehyde.

Lowering the current density either had no effect or resulted in lower conversions.

The change of structure of the cathode due to its casting temperature was important with cathodes of zinc and cadmium. A higher yield of the alcohol was obtained at the low temperature cast.

In general, electropolished surfaces were less active than others.

Highly active surfaces were obtained by treatment of the cathodes with nitric acid. Machined cadmium was affected the least. Renewal of the surface of the electrodes was found to be very important.

Results obtained with isobutyraldehyde were very

similar to those found with straight chain aldehydes by other investigators in that at room temperature the alcohol was the main product and that formation of hydrocarbon increased with the temperature.

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Determination of Hydrogen in Titanium¹

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ABSTRACT

A simple, rapid, precise method for determination of hydrogen in titanium is described. It is based on measurement of the equilibrium pressure of hydrogen over the metal in a closed system under predetermined conditions. Construction, calibration, and operation of the analytical equipment are described. Hydrogen can be determined in the range 0.001-0.33 wt % with a probable error of about 5%. The physical form of specimens is unimportant. Twenty analyses can be made in an 8-hr period.

INTRODUCTION

The chemical constitution and phase relationships of the titanium-hydrogen system at high temperatures have received attention from several investigators (1, 3-5, 8-10). Recently, McQuillan (6, 7) determined in great detail the pressure-temperature-concentration relationships for the titanium-hydrogen system in the range 450°-975°C. McQuillan's data indicate a continuous single phase in the condensed system where α or β titanium exists alone. Extrapolation of his curves would indicate very high solubility of hydrogen in titanium at room temperature. However, it was found (2) that solubility of hydrogen in titanium decreases markedly at temperatures below 200°C. Hydrogen in excess of the solubility limit precipitates, presumably as a hydride. The hydride precipitate in titanium or titanium-rich alloys seriously lowers the impact strength of the metal. Hence, control of the hydrogen level is of major importance in the manufacture, melting, fabrication, and subsequent use of titanium. Simultaneously it becomes highly desirable to have a simple, rapid, precise method for determination of hydrogen in titanium.

Available Analytical Methods

The most widely used techniques for determining hydrogen in titanium are the vacuum fusion method (11) and modifications involving temperatures short of fusion. In these methods hydrogen is quantitatively removed from the specimen by evacuation at high temperatures with subsequent analysis of the gases, usually in an integrated closed system. While such methods are capable of adequate precision, the apparatus required is rather elaborate and considerable time is required to outgas the furnace assembly either to a reproducible or to a negligible blank. Moreover, if gases other than hy-

drogen are evolved from the specimen, separation and analysis of the gases are necessary.

Another approach to hydrogen determination is via combustion in dry oxygen and gravimetric determination of the hydrogen as water. This method has shortcomings of a practical nature in that combustion is difficult to control and results generally lack the reproducibility and precision desired.

Principle of the Method

McQuillan's data indicate that, in single phase titanium under equilibrium conditions, dissolved hydrogen behaves as an ideal liquid, i.e., a linear relationship exists between the logarithm of the equilibrium pressure and reciprocal absolute temperature when the hydrogen concentration in the metal is held constant. Likewise, a plot of the logarithm of equilibrium pressure vs. the logarithm of concentration of hydrogen in the metal is linear under isothermal conditions. In regions where α and β titanium coexist, equilibrium pressure is independent of the hydrogen concentration in the metal as would be predicted from phase rule considerations. It has been established that hydrogen is the only common gas that, once dissolved in the metal, can be extracted to any measurable extent by temperature and pressure manipulation alone. Thus, determination of the equilibrium hydrogen pressure over a specimen of single phase titanium at a predetermined temperature for which the pressure-concentration relationship is known and in an apparatus of known volume affords data from which the hydrogen content of the metal can be readily calculated.

From a practical standpoint it is highly desirable to make these determinations in the β region for the following reasons.

1. The system is sluggish in attaining equilibrium conditions at low temperatures, whereas equilibrium is established very rapidly above the transition point (882°C).
2. The higher the temperature the higher the

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equilibrium pressure, increasing the relative precision with which pressure measurements can be made. It is true that the equilibrium pressure over α -titanium just below the transition point is greater than the equilibrium pressure over β -titanium at, say, 1000°C , concentration being constant. However, regions immediately in the vicinity of the transition point should be avoided for titanium specimens other than those of very high purity.

3. Many impurities stabilize a portion of the β structure well below the transition point. Hydrogen itself is a β -stabilizer. Therefore, the existence of single phase metal below the transition point cannot be universally assumed. On the other hand, the common α -stabilizers (oxygen, nitrogen, aluminum, and tin) must be present in much larger amounts than ordinarily found to effect any α -stabilization at 100°C above the normal transition temperature.

APPARATUS

All parts of the apparatus (Fig. 1) other than the sample tubes and heating sleeves are fabricated from borosilicate glass. Pressure is measured by means of the Todd Universal Gauge (A), a three-scale mercury gauge with a range of 0.0001 to 25 mm mercury. Bulb (B) is of approximately 250 ml capacity and is carefully calibrated for volume between stopcocks before attachment to the manifold. Tapered joint (C) permits attachment of other equipment to the bulb. Silica sample tubes (D) are connected to the manifold through 4 mm high vacuum stopcocks. Heating sleeve (E) is supplied with power by a 500 watt combination of a constant voltage transformer and variable transformer in tandem (F). Temperature is measured by means of a 20 gauge chromel-alumel thermocouple (G) and potentiometer (H). Evacuation is effected by means of a single stage mercury diffusion pump (I) with conventional mechanical forepump. Power to the heater of the diffusion pump is controlled by a 5 amp variable transformer (J); 4 mm stopcocks (K) and (L) permit isolation of the manifold from

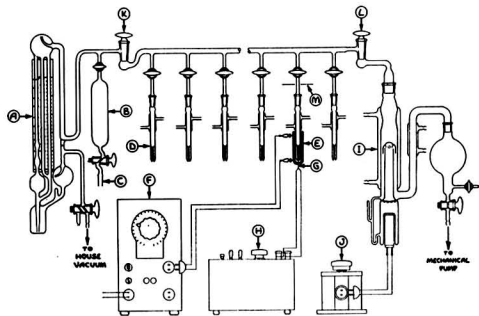


Fig. 1. Apparatus

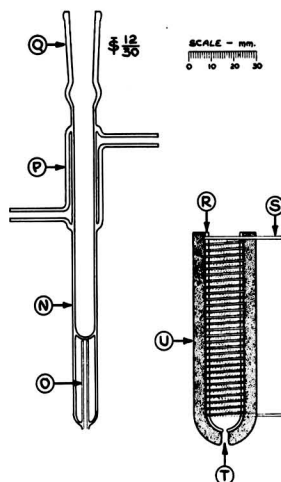


Fig. 2. Details of sample tube and heating sleeve

the gauge and from the pumping system. All stopcocks and tapered joints are hand-lapped to a fine finish. Stopcocks are lubricated with a highly refined vacuum grease with low thermal coefficient of viscosity, such as Apiezon N, and joints sealed with nongassing hard wax. Removable asbestos paper shields (M) protect the stopcocks from heat of the gas flame used in sealing and unsealing the hard waxed joints.

Details of a silica sample tube and heating sleeve are shown in Fig. 2. Sample tubes are fabricated entirely from transparent silica. The titanium sample rests on the bottom of the sample tube chamber (N). Sleeve (O) acts as a guide for the thermocouple, the hot junction of which touches the bottom of the furnace chamber. Thus the sample is separated from the thermocouple by only about 1 mm of silica. Chamber (P) provides for water cooling so that joint (Q) is kept at approximately room temperature. The water-cooled chambers of adjacent sample tubes are connected by short lengths of rubber tubing permitting in-line flow of cooling water. The heating sleeve consists of a silica shell (R) covered with thin asbestos paper and wound with 6 ft of $\frac{1}{32} \times 0.0035$ in. nichrome ribbon. The ends of the heating ribbon are joined to short lengths of heavy nichrome ribbon (S) which protrude from the shell to form lugs for connection to the power source through small battery clamps. A small opening (T) at the bottom of the sleeve provides access for the thermocouple. The wound sleeve is covered with a thermal insulating layer of macerated asbestos paper (U) $\frac{3}{16}$ in. in thickness. After bakeout, the exterior of the sleeve is painted with heat resistant aluminum paint. The inner diameter of the silica shell of the sleeve is approximately 1 mm greater than the outer

diameter of the sample tubes. A sample tube with heating sleeve in place is shown in Fig. 1. Approximately 2 ml of the sample tube volume is heated by the sleeve.

CALIBRATION

The purpose of the calibrated bulb (B) in Fig. 1 is to provide a means for determining the volume of the equipment. The procedure consists of partial evacuation of the system with the lower stopcock of the bulb closed, the upper stopcock open, and the stopcock to one sample tube open. Stopcock (L) is then closed and pressure measured by the gauge. The upper stopcock of the bulb is then closed, stopcock (L) is opened, and the system evacuated to a low pressure. This leaves a known volume of gas under a known pressure in the bulb. Stopcock (L) is then closed and the gas in the bulb is expanded to the evacuated system. Pressure is again determined. The volume of the apparatus (without the bulb which is normally not a part of the working volume) is then:

$$V_a = V_b \frac{P_1 - P_2}{P_2}$$

where V_a = volume of apparatus, V_b = volume of bulb, P_1 = initial pressure, and P_2 = final pressure (temperature assumed constant). This determination is then repeated at several pressure levels. The volume of the apparatus can be quickly determined with a probable error of less than 0.5%. The working volume of the apparatus is 400 ± 100 ml, depending on the number of sample tube connections and minor differences in construction details.

As previously discussed, it is highly preferable to operate in the β region. The operating temperature is ideally the highest readily attainable. However, this is moderated by several practical considerations. A temperature of 1000°C was selected as a compromise since: (A) It is sufficiently elevated above the normal transition temperature to guarantee single phase (β) titanium. (B) Reaction of titanium with the silica sample tube in the few minutes required at temperature is superficial, introducing negligible error due to contamination, and allowing reasonable sample tube life. It was found that the sample tubes remain operable for several hundred analyses. (C) Operating lifetime of nichrome heaters is reasonable. (D) Loss of hydrogen by diffusion through the silica is negligible in the short time required to attain equilibrium.

Determination of the equilibrium pressure-concentration relationship was made in the same apparatus later used for analyses. A few grams of titanium hydride was placed in a silica sample tube

and surmounted by a small plug of glass wool to prevent dusting. The tube was attached to the apparatus at joint (C) by hard wax. The hydride was thoroughly outgassed at room temperature, followed by heating to a moderate temperature where evolution of a minor amount of hydrogen helped to sweep out any remaining gases. After outgassing, the tube was never exposed to air during the equilibrium determinations. A 0.500 gram sample of commercially pure titanium sponge was placed in a sample tube which was hard waxed to the manifold. The titanium specimen was outgassed by heating at 1000°C and a pressure of approximately 10^{-5} . Outgassing under these conditions reduces the hydrogen content of the titanium to less than 3 ppm in 60 min. After outgassing, the sample tube was allowed to return to room temperature. Stopcock (L) was closed, isolating the system from the pumps and, with both stopcocks on bulb (B) open, the hydride tube was heated to generate hydrogen. When the desired hydrogen pressure had been attained, the upper stopcock on the bulb was closed and heating was discontinued. Hydrogen pressure and room temperature were observed. The titanium specimen was then heated to 1000°C and, when the system had attained equilibrium (less than 10 min over-all), room temperature and hydrogen pressure were again observed. From these observations and the known volume of the apparatus, one point of the equilibrium curve can be calculated:

$$\begin{aligned} H_o &= 2.02 \times \frac{P_1}{760} \times \frac{273}{T_1} \times \frac{V}{22,400} \\ &= 3.23 \times 10^{-5} \frac{P_1 V}{T_1} \end{aligned}$$

$$\begin{aligned} H_g &= 2.02 \times \frac{P_E}{760} \times \frac{273}{T_E} \times \frac{V}{22,400} \\ &= 3.23 \times 10^{-5} \frac{P_E V}{T_E} \end{aligned}$$

$$H_T = H_o - H_g$$

$$C_E = \frac{H_T}{S} \times 100$$

where: H_o = hydrogen introduced, grams; H_g = gaseous hydrogen at equilibrium, grams; H_T = hydrogen in the titanium sample at equilibrium, grams; C_E = concentration of hydrogen in titanium at equilibrium, wt %; P_1 = initial hydrogen pressure, mm Hg; T_1 = room temperature, $^\circ\text{K}$, at P_1 ; P_E = equilibrium hydrogen pressure, mm Hg; T_E = room temperature, $^\circ\text{K}$, at P_E ; V = volume of apparatus, ml; and S = weight of titanium specimen, grams.

The titanium was then outgassed and the cycle

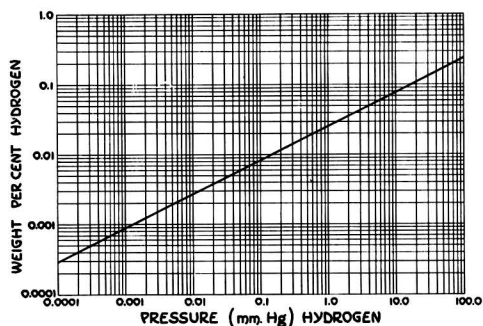


Fig. 3. Equilibrium curve for titanium-hydrogen at 1000°C.

repeated at 12 levels of equilibrium hydrogen pressure in the range 0.001–10 mm Hg. A plot of the equilibrium pressure vs. concentration at 1000°C is shown in Fig. 3. The mean deviation of points from the curves is less than 2%. Repeat measurements with ingot and sheet of commercial purity showed that equilibrium values for these materials fell on the same curve. Impurities within the commercial range of concentration do not materially affect the equilibrium. The slight deviation from the theoretical slope of $\frac{1}{2}$ is believed to be a systematic error.

ANALYTICAL PROCEDURE

Specimens to be analyzed should be in the range 0.4–0.6 gram and are weighed to ± 0.01 gram. The physical form of samples is relatively immaterial; samples may be in the form of sponge, solid pieces of ingot or sheet, drillings, turnings, shavings, or finely divided metal. Bulky samples, i.e., fine turnings, should be compacted by pressing. Samples are placed in individual sample tubes which are attached to the manifold with hard wax. If less than a full complement of sample tubes is attached to the manifold, it is advisable to cap off the remaining joints to minimize the possibility of leaks. The system is evacuated at room temperature to an ultimate pressure of about 10^{-4} . The pressure in the system is observed and, with all stopcocks to sample tube open, stopcock (L) is closed. After 10 min the pressure is again observed. If the final pressure is 5×10^{-4} or lower, the error introduced by leaks will be negligible if the hydrogen content of samples is above 20 ppm. All stopcocks to the sample tubes are then closed with the exception of #1 tube. With heater and thermocouple in place, the tube is heated to 1000°C in 6–7 min and held to $\pm 2^\circ\text{C}$ to the end of 10 min from start of heating. Room temperature and hydrogen pressure are then observed. Heating is discontinued, the stopcock to #1 tube closed and #2 opened. The system is evacuated to about 10^{-4} and the analytical cycle repeated for the second specimen. Successive samples are treated in the

same fashion. Equilibrium pressures can be determined in a single apparatus at the rate of four per hour.

Calculation of the hydrogen content of a specimen involves, for the general case: (a) estimation of the equilibrium hydrogen concentration, C_E , from the curve (Fig. 3); (b) calculation of the hydrogen in the gas phase at equilibrium from observed pressure and room temperature and known volume of the apparatus; (c) summation of the hydrogen in the gaseous and condensed phases and conversion to per cent hydrogen in the original specimen:

$$\begin{aligned} \%H &= C_E + 2.02 \times \frac{P_E}{760} \times \frac{273}{T_E} \times \frac{V}{22,400} \times \frac{100}{S} \\ &= C_E + 3.23 \times 10^{-3} V \frac{P_E}{T_E S} \\ &= C_E + K \frac{P_E}{T_E S}, \quad \text{where } K = 3.23 \times 10^{-3} V \end{aligned}$$

An estimation of the probable errors in the various factors and their influence on the accuracy of the analysis indicates their relative importance and points out some justifiable short-cuts when ultimate accuracy is not required. The values for maximum error in Table I were derived with the following assumptions of accuracy of measurement of the individual factors: (A) Specimen temperature at equilibrium is $1000 \pm 2^\circ\text{C}$. (B) Values of C_E as derived from P_E (Fig. 3) are $\pm 1\%$. (C) Equilibrium pressure is measurable to within one scale division. This amounts to $\pm 20\%$ at 0.001 mm, $\pm 0.4\%$ at 25 mm. (D) The volume of the apparatus is known to $\pm 1\%$. (E) Room temperature is measured to $\pm 1^\circ\text{C}$. (F) The weight of the titanium specimen is known to 0.01 gram.

Nominal values used in the calculations are $V = 400$ ml, $T_E = 300^\circ\text{K}$, and $S = 0.50$ gram.

The greatest individual source of error is the uncertainty in the measurement of P_E . It is also apparent that for low hydrogen concentrations the hydrogen in the gas phase at equilibrium may be generally regarded as negligible. Per cent H = C_E may be assumed up to concentrations of 0.0030% with an error of 0.0001% or less, i.e., about equal to the error introduced by uncertainty in the value of P_E .

TABLE I

P_E	% H	C_E	$K \frac{P_E}{T_E S}$	Error, % H	% Error
0.001	0.000873	0.000864	0.000009	0.000094	10.8
0.01	0.00269	0.00260	0.00009	0.00016	5.9
0.1	0.00888	0.00801	0.00087	0.00035	3.9
1	0.0331	0.0244	0.0087	0.0014	4.2
10	0.1609	0.0741	0.0868	0.0046	2.9
25	0.331	0.116	0.215	0.010	3.0

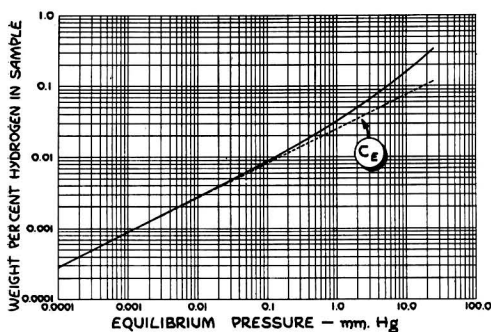


FIG. 4. % H vs. P_E at 1000°C. $V = 400$ ml; $T_E = 300^\circ\text{K}$; and $S = 0.50$ g.

If the sample weight and room temperature are held constant, the per cent hydrogen in the sample will be a function of the equilibrium pressure alone. Small variations in T_E introduce negligible error. Therefore, if S is held constant, T_E varies only a few degrees, and V is known, it is possible to draw a curve interrelating % H with P_E . The curve allows estimation of % H directly from the equilibrium pressure reading with an expected error of less than 10%. A family of such curves permits interpolation for variations in sample weight. A plot of % H vs.

TABLE II. Comparative results by equilibrium and vacuum fusion methods

Sample No.	Equilibrium method	Vacuum fusion method	Difference
1	0.0017	0.0015	+0.0002
2	0.0037	0.0042	-0.0005
3	0.0047	0.0049	-0.0002
4	0.0071	0.0067	+0.0004
5	0.0098	0.0101	-0.0003
6	0.0103	0.0106	-0.0003
7	0.0242	0.0234	+0.0008
8	0.0402	0.0387	+0.0015
9	0.0861	0.0840	+0.0021
10	0.182	0.183	-0.001
11	0.304	0.316	-0.012

P_E is shown in Fig. 4 in which nominal values of $T_E = 300^\circ\text{K}$ and $S = 0.50$ gram are used.

After analyses have been completed, sample tubes are removed from the manifold, the titanium specimens discarded, and the tubes cleaned by digestion in warm 10% HCl. After rinsing with water and methanol and oven drying, the tubes are ready for reuse.

ACCURACY AND REPRODUCIBILITY

Several samples of closely sized titanium sponge covering a wide range of hydrogen contents were prepared by exposing the sponge to hydrogen at about 400°C. After the desired amount of hydrogen had been added, samples were heated in a closed system at 600°C for several hours to promote homogeneity. Samples of the sponge were then analyzed for hydrogen by the equilibrium method and by the vacuum fusion technique as a reference method, each analysis being made in triplicate. Average results are shown in Table II.

Another set of sponge samples, similarly prepared, was subjected to multiple analyses by the equilibrium method to ascertain the reproducibility of the method. Results are given in Table III.

These results indicate the reliability of the method in regard to accuracy and reproducibility. Equilibrium method results are in good agreement with those obtained by vacuum fusion. The average deviation is 3.3% when the hydrogen content is above 0.005%. Random interchange of direction of difference indicates continuity of basic agreement between the two methods within the range investigated. Results in general follow the pattern of error calculations presented in Table I although the most deviant results indicate the possibility of somewhat greater error in single determinations. Reproducibility results may be looked upon as "minimum reproducibility" since deviations may be partially due to minor inhomogeneity in the sponge. Consideration of results of the two sets of tests indicates

TABLE III. Reproducibility of results by the equilibrium method

	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
	0.0016	0.0027	0.0100	0.0254	0.0397	0.340
	0.0015	0.0032	0.0102	0.0241	0.0402	0.308
	0.0019	0.0027	0.0108	0.0220	0.0412	0.316
	0.0020	0.0029	0.0101	0.0248	0.0396	0.337
	0.0018	0.0032	0.0105	0.0236	0.0407	0.306
	0.0018	0.0030	0.0102	0.0239	—	0.301
	0.0020	0.0028	0.0110	0.0242	—	0.322
	0.0016	0.0028	0.0106	0.0255	—	0.325
	0.0014	0.0031	0.0107	0.0243	—	—
	0.0018	0.0030	0.0104	0.0247	—	—
Avg.....	0.00174	0.00294	0.01045	0.02425	0.0403	0.319
M.D.....	0.00017	0.00016	0.00027	0.00070	0.00054	0.0116
%M.D.....	10	5.4	2.6	2.9	1.3	2.8

TABLE IV. Probable errors of single hydrogen determinations

Hydrogen level	Probable error
0.001-0.01	0.0003
0.01-0.02	0.0006
0.02-0.05	0.0012
0.05-0.1	0.0025
0.1-0.2	0.005
0.2-0.3	0.01

the approximate pattern of probable errors in single determinations by the equilibrium method as shown in Table IV.

From this the probable per cent error in a single determination is 5% or less, provided the hydrogen content is above 0.006%. At lower hydrogen levels the probable per cent error increases to about 30% at 0.001% hydrogen.

These tests were made on specially homogenized sponge but, in actual analyses, the hydrogen usually is less uniformly dispersed. This is particularly true of fabricated metal where it is not uncommon to find 20% variations in hydrogen content, depending on the site of sampling.

In obtaining the data presented in Table II it was found that the reproducibility of the equilibrium method is about double that of the vacuum fusion technique even when extraordinary care is used in applying the latter method. This has been substantiated by subsequent comparative analyses on ingot and sheet samples of commercially pure titanium.

ANALYSIS OF TITANIUM-RICH ALLOYS

Tests have shown that this method can be applied to the determination of hydrogen in titanium-rich alloys. Specimens of 4% Mn-4% Al and of 7% Mn commercial titanium alloy sheet were prepared with a number of hydrogen concentration levels by introducing or removing hydrogen by heating specimens under hydrogen or in vacuum. Samples of each specimen so prepared were analyzed in triplicate by vacuum fusion and by the equilibrium method using C_E values established for commercially pure titanium. Results are shown in Fig. 5 and 6. The linearity of comparative results obtained by the two methods indicates that, at least within the hydrogen concentration range investigated, the equilibrium method is adapted to the determination of hydrogen in these two alloys. It is necessary, when using equilibrium data for commercial titanium, only to multiply the result by factors of 0.80 and 0.76, respectively, to obtain per cent hydrogen in the alloys. Since the conversion factors are close to unity, minor changes in the percentage constitution of the alloy introduce little error. Of course, C_E vs. P_E and % H vs. P_E curves could be established for alloys as for the commercially pure metal. It

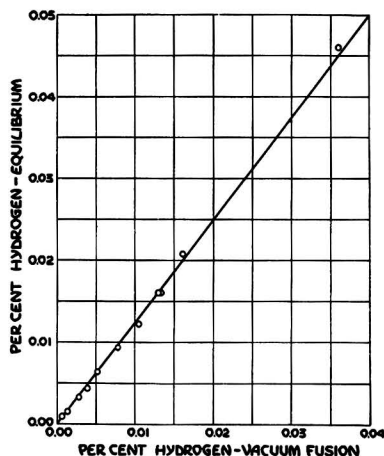


Fig. 5. Hydrogen analysis of 4% Mn-4% Al alloy

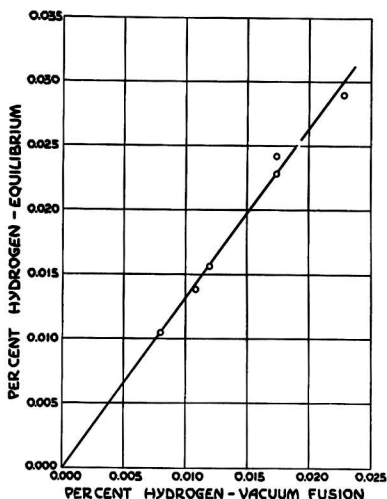


Fig. 6. Hydrogen analysis of 7% Mn alloy

is probable that most titanium-rich alloys can be treated in the same manner.²

DISCUSSION

The analytical apparatus described has a large number of vacuum stopcocks. Stopcocks were used in setting up the apparatus for trial with the expectation of replacing them with mercury cut-offs if the method proved successful. However, it was found that by careful lapping and greasing, the stopcocks provide adequate sealing and no trouble is encountered by outgassing of the lubricant in the pressure range for which the method is adapted.

² This method may also be applied to 5% Sn-2.5% Al alloy, using a factor of 0.60. Thus the method is applicable to the determination of hydrogen in the three general alloy systems: α - β , α -strengthened α - β , and α -stabilized.

The theoretical range of the method as described is 0.0003–0.33% hydrogen. Samples have been analyzed in the range 0.0008–0.31% hydrogen. Lower hydrogen concentrations down to about 0.00001% hydrogen can be determined by replacing the Todd gauge with a sensitive McLeod gauge. However, this would almost certainly also involve replacement of the stopcocks with mercury cut-offs and recourse to much more complete outgassing of the equipment before determination of the equilibrium pressure. Concentrations higher than about 0.3% can be determined by replacing the gauge with a manometer. Determination of the equilibrium curve for equilibrium concentrations greater than 0.15% hydrogen would have to be determined since the curve ceases to be linear.

The sample size has no practical bearing on the accuracy of the analysis provided equilibrium conditions are maintained. Therefore, there is little to gain by using a large specimen other than the possibility of obtaining a more representative sample. Sample size selection is guided, therefore, by the optimum size of silica sample tubes for ease of fabrication with vacuum-tight welds. The specification of 0.5 ± 0.1 gram samples is made in the interest of maintaining a fairly constant geometric relationship between sample and sample tube.

Errors due to outgassing of the equipment have proved to be no problem. Normally the pressure rise, due to outgassing and leaks, in a 10-min period at room temperature is less than 0.5μ . Thus it appears that adsorbed gas remaining after evacuation of the glassware is tightly enough bound to preclude any considerable outgassing in the short analytical period. Blank determinations with empty sample tubes give a pressure rise of less than 1μ . This is due almost entirely to outgassing of the heated section of the sample tubes. A 1μ pressure rise corresponds to approximately 50 monolayers of adsorbed water on the walls of the sample tube. In an actual determination, the hot specimen getters a portion of any desorbed oxygen or nitrogen. The error introduced by desorption of water from the walls of the sample tube is of the order of 0.00015% hydrogen at the 0.0010% hydrogen level, 0.00005% at the 0.0025% level, and is entirely negligible at higher levels.

The determination as described is a measure of the hydrogen content of the metal plus any hydrogen retained as water after evacuation. Adsorbed water that cannot be removed by evacuation is negligible unless the sample has very high surface. Water associated with residual salts in sponge is another possible hydrogen reservoir but has been found to be negligible if the sponge has been properly vacuum distilled during manufacture.

Sample tubes can be heated to 1000°C in 6–7 min.

Establishment of equilibrium is very rapid. A total heating time of 10 min, i.e., 3–4 min at 1000°C, is specified to insure reproducible thermal conditions in the heated sample tube. Specimens held at temperature for times up to 30 min showed no drift in the equilibrium pressure.

It is important that the equilibrium pressure of samples be measured under the same thermal conditions for which the equilibrium curve was established.

The portion of the sample tube that is heated to 1000°C represents only about 0.5% of the total volume of the apparatus. Treating the apparatus as an isothermal unit for mathematical purposes is justified since the error introduced in doing so is very small.

The sample tube connections on the manifold may be any number between 1 and 20, depending on the volume of analyses to be performed.

Whether analytical results should be calculated by summation of $C_E + K (P_E/T_E S)$ or read directly from a % H vs. P_E plot (Fig. 4) is dependent on the uniformity of samples and the precision desired. For samples of low hydrogen content the relationship % H = C_E is valid within the accuracy of the method.

Experience has shown that an analyst familiar with the method can perform twenty analyses per day on a routine basis with a single apparatus.

This method is applicable to analysis of other metals for which an equilibrium hydrogen concentration-pressure relationship can be established.

ACKNOWLEDGMENT

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

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Influence of Impurities in the Electrolyte in Chlorine-Caustic Electrolysis by the Mercury Cell Process

IV. Investigation of the Influence of Metals on the Cathodic Current Efficiency¹

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ABSTRACT

An electrolysis cell for laboratory use with circulating brine and mercury was constructed. With this cell the effect of a number of metals upon cathodic current efficiency was studied, among which vanadium, molybdenum, chromium, and titanium proved to be the most harmful ones.

INTRODUCTION

In previous papers (1-3) results were reported from a number of experiments with NaCl solution contaminated with various metal salts and shaken with sodium amalgam. The purpose of those experiments was to investigate the influence of impurities on the amalgam decomposition rate. Results were expected to be of great value for predicting the effect of contaminations in a mercury cell with sodium amalgam cathode, even though conditions are quite different in the two cases.

However, results from amalgam decomposition experiments had to be confirmed by electrolysis experiments in order to provide the chlorine caustic industry with reliable information concerning the influence of various impurities. Thus, a mercury cell suited for laboratory scale electrolysis experiments had to be constructed. The laboratory cell, made by Walker and Paterson (4), was considered unsuitable because it used noncirculating mercury as cathode.

The object was to reproduce the construction and working properties of the industrial mercury cell as well as possible on a smaller scale. Consequently, the cell had to be long and the mercury layer comparatively thin. Calculations showed that, if the proper scale was used, the depth of mercury should be only 0.2 mm with 300 mm cell length, in order to give the same mercury flow rate as in full size. So thin a film is quite impossible to obtain in a glass apparatus; it is even difficult to obtain a coherent mercury layer thinner than 1-1.5 mm.

Furthermore, the cell temperature had to be about 70°C, corresponding to normal working temperature in industrial practice. Preparatory experiments in a cell consisting of a 400 mm glass tube showed that the heat generated by the cell resistance is far from sufficient to maintain this

temperature, so a preheater for the brine was provided.

DESCRIPTION OF CELL

The cell construction was unrestricted except that circulating mercury had to be used to obtain interpretable results, and for continuous operation it was necessary to supply fresh concentrated brine to the cell.

A basin-shaped glass cell (Fig. 1) was supplied with inflow tubes for mercury and brine. Mercury left the cell through a centrally placed overflow pipe. This was extended below the cell and there formed a lock, which prevented the brine from running off with the mercury.

Current was supplied to the mercury by a platinum wire. The anode consisted of a circular platinum sheet provided with a number of holes to facilitate escape of the chlorine. The cell could also be operated with a graphite anode to test various graphite properties.

The cell was closed by a rubber stopper which also carried the anode. Chlorine and spent brine left the cell through an outlet tube which opened at the lower surface of the stopper. There was also space for a thermometer and capillaries for polarization measurements.

The cell was safe in operation and extremely easily cleaned, which was of great importance in experiments with contaminated salt solutions. These experiments were often of comparatively short duration and required an exceedingly careful cleaning after each experiment to give reproducible results.

Auxiliary Equipment

A sketch of the complete apparatus is given in Fig. 2. Mercury ran from storage bottle A to a level

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assumption that hydrogen evolution was the only loss reaction at the cathode, which is probably the case at high current efficiencies. The two methods for determining current efficiency gave coinciding results, except for experiments with low current efficiencies, in which the gas analysis method gave values which seemed to be a little too high.

For analysis of the cell gas, a volume corresponding to about one minute of electrolysis was collected in concentrated sodium hydroxide in a gas burette. Finally, the volume of the hydrogen gas was recorded. In order to avoid errors due to varying brine volume in the cell, the brine circulation was interrupted during the analysis period. The mercury was, however, circulated continuously.

Before an experiment was started, the storage bottle was charged with 2-4 l saturated, filtered brine, which had been mixed with the impurity to be studied. After the cell was filled with brine and the correct flow rate reached, the current was switched on.

During the experiment the mercury and brine flow were repeatedly controlled. The analysis of departing mercury was made at suitable intervals. By observation of gas evolution at the cathode surface current efficiency could be approximately estimated. When it was seen that the current efficiency was changing rapidly, the amalgam or cell gas was analyzed as frequently as possible while, in other cases, analyses were performed at longer intervals.

After each experiment the apparatus was carefully cleaned and the electrolysis cell washed with concentrated hydrochloric acid and rinsed with distilled water.

The mercury was purified when it had been polluted with certain noble metals by shaking with soft paper. The polluting metals were oxidized and absorbed by the paper, after which it was filtered through a punctured paper cone. When this procedure had been repeated two or three times, the mercury was pure enough to be used again in electrolysis experiments.

The investigation included experiments with vanadium, molybdenum, chromium, titanium, magnesium, calcium, barium, aluminum, iron, nickel, copper, zinc, lead, arsenic, and manganese. These were assumed to occur, ordinarily or exceptionally, in industrial brines.

In order to test the apparatus, a great number of experiments with pure sodium chloride solutions were performed, giving an average current efficiency of 98.5-99.2%.

Vanadium.—Previously (1-3) vanadium proved to be one of the most harmful metals; hence it was more thoroughly investigated than other impurities.

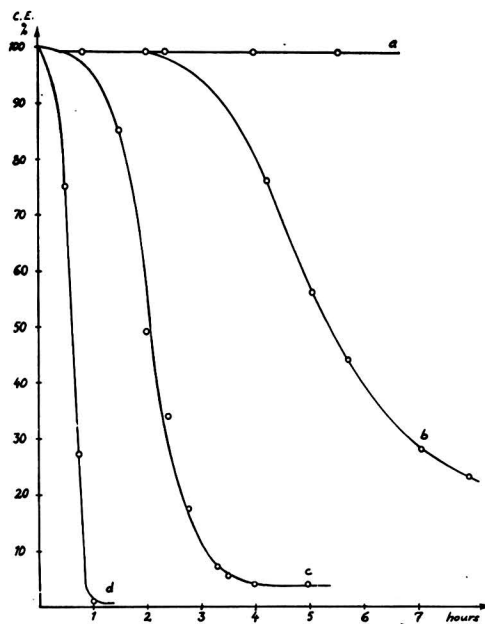


FIG. 3. Current efficiency in presence of vanadium. Curve a, 0.1 mg/l V; curve b, 0.25 mg/l V; curve c, 0.5 mg/l V; curve d, 1.7 mg/l V.

Reproducibility of these experiments was not so good, and many of them had to be repeated several times. Fig. 3 shows some representative current efficiency curves from experiments with vanadium concentrations, ranging from 1.7 to 0.1 mg/l in the brine supplied.

In all of these experiments the mercury surface was partly covered with a "gas spot," from which the gas emanated. The size of this spot grew as the current efficiency decreased, and finally covered the cathode completely. (The current efficiency had then usually decreased to 4-5%.)

In most experiments, part of the spot occasionally flaked off and departed from the cell with the mercury. This may explain the lack of reproducibility.

The experiments show that vanadium greatly reduces cathodic current efficiency. The higher the vanadium concentration, the greater the decrease. With 1.7 mg/l vanadium practically only hydrogen gas is formed, whereas with 0.1 mg/l vanadium no decrease in the current efficiency can be observed even after 7 hr.

A few additional experiments with a single (non-recurrent) addition of a certain quantity of vanadium (as sodium metavanadate solution) to the pure brine were performed in order to make clear whether the action of a certain quantity of vanadium was

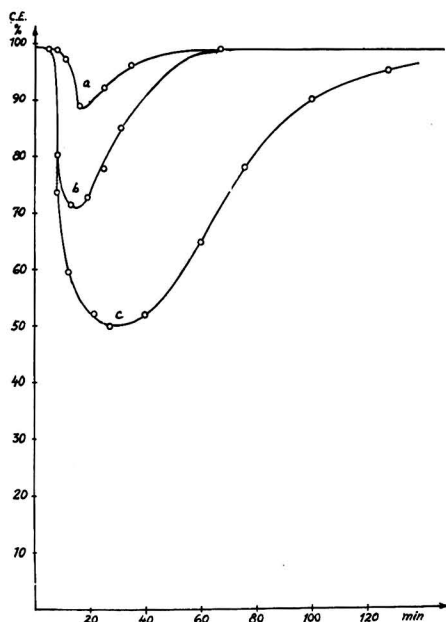


Fig. 4. Current efficiency after addition of a certain quantity of vanadium. Curve a, 0.05 mg V; curve b, 0.1 mg V; curve c, 0.2 mg V.

permanent or if it ceased when the supply of vanadium to the cell was cut off.

Results of these experiments are demonstrated by curves in Fig. 4 and show that vanadium does not remain very long in the electrolysis cell. The problem of whether its removal can be performed by successive replacement of vanadium-containing brine with pure brine or by deposition of metallic vanadium at the mercury surface cannot be definitely solved by these experiments, but will be discussed later.

There is, however, some evidence that the "gas spots," mentioned previously, consist of interfering metals in the reduced form and that vanadium is thus removed from the cell with the mercury. In the latter experiments, the mercury circulation rate was about 3.5 times the usual one, i.e., 28 ml/min, in order to facilitate any possible mechanical removal of vanadium. The brine supply rate was maintained at 7.5 ml/min.

Molybdenum.—In industrial brines molybdenum will probably not occur ordinarily, but as a complement of the amalgam decomposition experiments, this metal was also investigated. Results are represented in Fig. 5.

The curves show that molybdenum also caused a considerable hydrogen evolution in the electrolysis experiments.

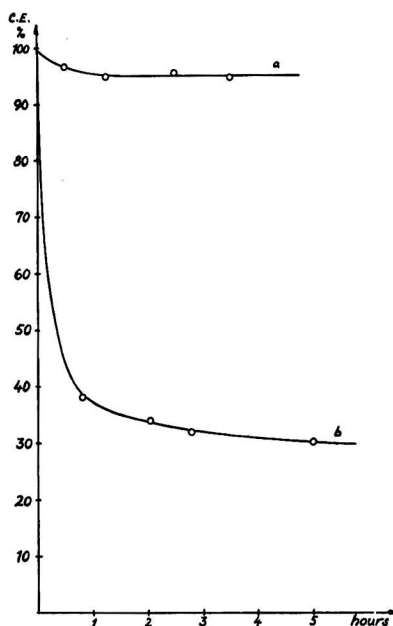


Fig. 5. Current efficiency in presence of molybdenum. Curve a, 0.5 mg/l Mo; curve b, 1.5 mg/l Mo.

In these experiments also gas evolution was found to take place at one spot on the mercury surface.

Chromium.—In the previous amalgam decomposition experiments, it was found that chromium belongs to the same group of harmful metals as vanadium but that its influence depends on the pH. In alkaline solutions chromium is very harmful, while in acid solutions the influence is moderate. It may be expected, therefore, that chromium causes comparatively small gas evolution at first, when the brine is slightly acid, but that the influence is greater with pH increase of hydrogen ion deposition.

Chromium was added as chromium sulfate. Results are represented in Fig. 6. The curves show that chromium strongly decreases the cathodic current efficiency, and that even 0.25 mg/l Cr has a considerable influence.

So it may be concluded that vanadium, chromium, and molybdenum cause a very great reduction of the cathodic current efficiency. Thus, results gained from the amalgam decomposition experiments are fully verified by the electrolysis experiments. It is also remarkable that all of these metals, at least in moderate concentrations, cause hydrogen evolution from only a limited part of the cathode surface.

Titanium.—In the amalgam decomposition experiments (1-3), titanium caused a somewhat increased decomposition rate. In the electrolysis experiments this metal behaved very remarkably.

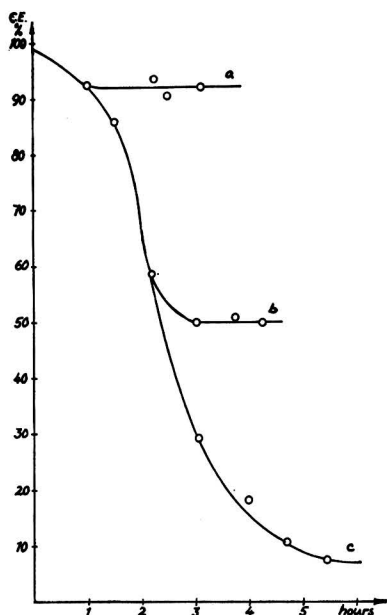


FIG. 6. Current efficiency in presence of chromium. Curve a, 0.25 mg/l Cr, curve b, 0.5 mg/l Cr; curve c, 1.5 mg/l Cr.

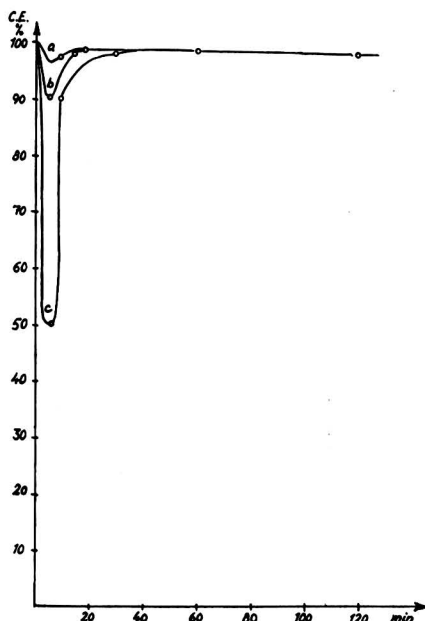


FIG. 7. Current efficiency in presence of titanium. Curve a, 0.1 mg/l Ti; curve b, 1.0 mg/l Ti; curve c, 5.0 mg/l Ti.

As soon as the current was switched on, the cathode was covered with small gas bubbles. With higher concentrations of titanium, a dark spot was formed at which the gas evolution took place. After a few minutes the spot diminished in size, and after about 15 min of electrolysis the cathode was quite bright again and current efficiency had been restored to 98–99%. Current efficiency curves for 0.1, 1, and 5 mg/l Ti are shown in Fig. 7.

Titanium in concentrations of 1–5 mg/l caused still another effect. When the brine flow rate was increased ten times, a dark spot appeared in a few minutes. The surface was soon completely covered simultaneously with a decrease of the current efficiency to about 30%. When the normal brine circulation rate was restored, the spot disappeared, and the cathode was again bright in a few minutes.

This effect was not obtained with vanadium (0.1 mg/l) or aluminum (5 mg/l).

Magnesium.—In concentrations below 25 mg/l magnesium did not interfere with amalgam decomposition (1–3), but in the electrolysis experiments some interesting observations were made. In the presence of magnesium at concentrations above 5 mg/l, current efficiency was slightly decreased from about 98.7% to about 97.1%. During electrolysis, a thin layer of hydroxide or possibly a mixture of hydroxide and magnesium amalgam was formed at the cathode surface. In this case, hydrogen

evolution did not occur at a single spot, but was distributed over the whole of the mercury surface.

Furthermore, mercury circulation was, in many cases, disturbed in such a way that amalgam accumulated in the cell, thus giving a seemingly strong decrease of the current efficiency. After a certain time the film was partly destroyed and removed from the cell. Current efficiency then seemed to be greater than 100%. Fig. 8 shows a typical current efficiency curve which is based on amalgam analyses. The cell gas analyses, however, showed an approximately constant value of about 97%.

Calcium.—In amalgam decomposition experiments, calcium had no influence at concentrations up to 25 mg/l. Electrolysis experiments confirmed this result, and 10 mg/l Ca in the brine caused no decrease of current efficiency within 3 hr.

Barium.—With barium the same result was obtained; 10 mg/l Ba did not affect current efficiency.

Aluminum.—It was found that aluminum accelerated amalgam decomposition (1–3). Also, in electrolysis experiments, hydrogen gas evolution occurred, and immediately after the start of an experiment, small gas bubbles were formed all over the mercury surface. A few minutes later a dark spot appeared, at which the gas evolution was concentrated. The spot grew very quickly and soon covered the whole cathode surface. However, after about 15 min of electrolysis gas evolution decreased again, and after half an hour it had ceased com-

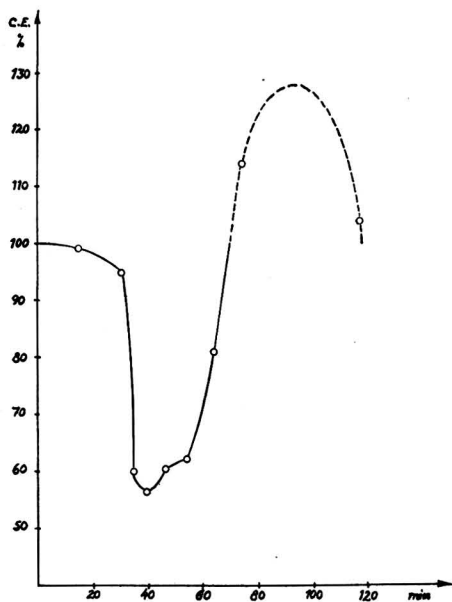


FIG. 8. Current efficiency in presence of 5 mg/l magnesium as indicated by amalgam analyses.

pletely. The mercury cathode was then quite bright, and the current efficiency was 98–99%.

The same cycle was repeated about 15 min later, as shown in Fig. 9. Reproducibility was not very good, but the tendency is quite clear. The experiments show that current efficiency is decreased by aluminum in concentrations greater than 1 mg/l. Thus the metal must be regarded as harmful, although not belonging to the same class as vanadium.

Iron.—In amalgam decomposition experiments, iron was found to affect the decomposition rate very slightly. Electrolysis experiments also showed that iron has no influence on cathodic current efficiency when the iron concentration does not exceed 10 mg/l.

Nickel.—In concentrations below 25 mg/l this metal had no influence on current efficiency.

Copper.—In concentrations below 10 mg/l, copper proved to have no effect on cathodic current efficiency in electrolysis experiments of normal duration. However, the metal was not oxidized in the amalgam decomposition tower, but was accumulated in the mercury system, thus giving rise to disturbances when the comparatively low solubility limit had been reached and pure copper was deposited at the cathode.

Zinc.—With 25 mg/l Zn in the brine the current efficiency was 98.9–99.3%, which is in good agreement with amalgam decomposition experiments.

Lead.—In concentrations below 25 mg/l, this

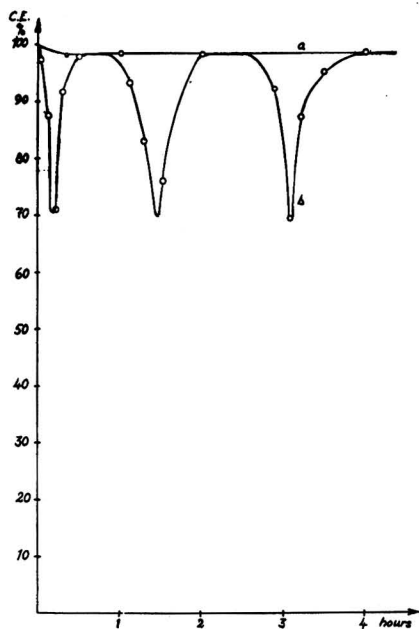


FIG. 9. Current efficiency in presence of aluminum. Curve a, 1 mg/l Al; curve b, 25 mg/l Al.

metal had no direct influence on current efficiency. It should be noted, however, that lead salts are able to precipitate certain harmful metals, such as vanadium, molybdenum, and chromium, and may therefore be used for purification of brines containing these metals (5).

Arsenic.—The influence of arsenic was studied in concentrations up to 25 mg/l. No decrease of the current efficiency was observed, although this metal had previously been proved to interfere with the amalgam decomposition.

Manganese.—With sodium chloride solutions containing 5–25 mg/l manganese, current efficiency was even somewhat higher than normal, 99.3–99.8%. In the electrolysis, Mn^{2+} was oxidized to MnO_2 which was deposited at the anode and increased the cell voltage.

SUMMARY

A mercury cell with circulating brine and circulating mercury is described, and results from a series of experiments with this cell are reported. It has been shown that:

1. Vanadium, molybdenum, chromium, and titanium cause very strong hydrogen gas evolution and thus decrease cathodic current efficiency considerably.

2. Magnesium and aluminum interfere with

cathodic reactions and may decrease current efficiency.

3. Calcium, barium, iron, nickel, copper, zinc, lead, arsenic, and manganese have no influence upon the cathodic current efficiency when they are in low concentrations and not mixed with other metals.

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

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Electrochemical Behavior of a Titanium-Fused Salt-Platinum Cell¹

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ABSTRACT

The cell, Ti/NaCl or KCl fused/Pt at temperatures above 800°C and in air, displays a substantial open-circuit potential difference of 1.40–1.53 v. In vacuum or under an inert gas the difference is approximately 0.5 v, and the current that can be drawn from such a cell is low. Air, oxygen, and water vapor act as cathodic depolarizers, maintaining a positive potential of the cathode and an appreciable current if the cell is short circuited. The reaction occurring in the cell is $\text{Ti} + 4\text{NaCl} + \text{O}_2 = \text{TiCl}_4 + 2\text{Na}_2\text{O}$. Alkali oxides are produced on the cathode if a salt containing Ti ions is electrolyzed in presence of air. Under an inert gas the discharge of alkali ions hampers the deposition of Ti, which is then produced in the form of a powder, and possibly as the result of a secondary reaction wherein it is reduced by the alkali metals.

INTRODUCTION

It is well known that it is extremely difficult to deposit titanium even from molten salt baths with an external current; the metal may be deposited under an inert atmosphere in the form of powder, flakes, or as a very thin layer (1), but no deposition is observed if air (oxygen) is present to any appreciable extent.

It would be of value to know the reasons for this behavior, and to determine the action of air and moisture during electrolysis. Such knowledge might furnish clues to the successful solution of the problems of the electrodeposition of titanium.

One of the obstacles to the electrodeposition of titanium in the presence of air is the high susceptibility of this metal to oxidation, and to corrosion in molten salts at elevated temperatures (2). Titanium, if deposited on the cathode, may disperse in the molten salt because of pyrosol formation, thus retarding the deposition process. However, it is doubtful if pyrosol formation is the chief deterrent to the deposition of the metal, especially if the cathode is capable of forming a solid solution with titanium. The fact that, in the presence of air or moisture, no titanium is cathodically deposited points toward other electrochemical or chemical events which hamper electrodeposition.

The behavior of the cell Ti/fused salt/Pt in various gases and in the presence of water vapor gives some answers to the problems of deposition.

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EXPERIMENTAL PROCEDURE

A preliminary experiment showed that a cell consisting of titanium and platinum electrodes immersed in molten sodium chloride produced a fairly strong current if the electrodes were short circuited through a milliammeter. The direction of the current indicated that titanium went into solution acting as an anode with the platinum as the cathode.

In order to explore this phenomenon in detail a cell was constructed which made it possible to accumulate separately the anodic and cathodic reaction products for subsequent analysis. Copper tubing was also provided for introducing gases and steam into the cathodic compartment. The arrangement is shown in Fig. 1. Air had access to the crucible in the furnace, although a loose cover was made from a piece of fire resistant brick.

To determine the influence of air (oxygen), arrangement was made to heat the crucible C (Fig. 1) in vacuum or in an inert gas, and simultaneously to measure the emf of the open cell or the current delivered by a closed cell. This was accomplished by placing the crucible together with the electrodes and salt in a quartz glass tube, as shown in Fig. 2. The lower part, C, of this apparatus was placed into the furnace (Fig. 1).

The operating procedure was as follows: the temperature of the furnace was raised to 880°C or higher to melt completely the salts, and then lowered to the working temperature of 850° or 800°C, which is above the melting point of the 50–50 mole per cent KCl-NaCl mixture. Some runs were made in pure sodium chloride and some in pure potassium chloride. Measurements of the emf of the Ti/molten salt/Pt cell were continued until this force became approximately constant. Then the switch, S, (Fig. 1)

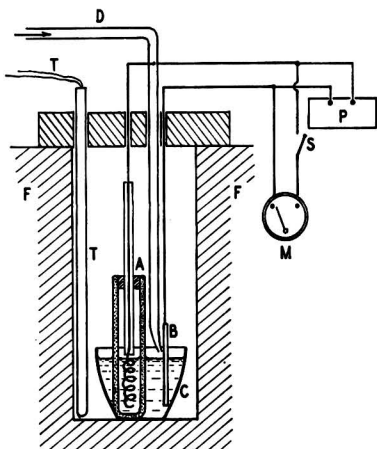


FIG. 1. Arrangement of the Ti/salt/Pt cell for emf and current measurements. (A) Ti wire anode in a porous Al_2O_3 thimble with the top open or closed; (B) Pt cathode (3 cm^2); (C) porcelain crucible containing alkali salt or mixture of salts; (D) copper tubing for gas introduction; (F) resistance furnace; (M) milliammeter; (P) potentiometer; (S) switch; (T) thermocouple.

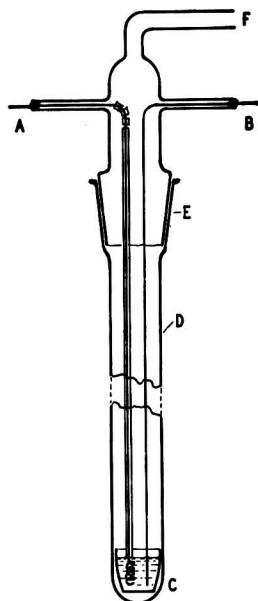


FIG. 2. Arrangements of the Ti/fused salt/Pt cell for emf and current measurements under a protective atmosphere. (A, B) Leads to potentiometer or milliammeter; (C) crucible with salt bath; (D) tube of quartz glass; (E) joint; (F) connection to vacuum and gas supply.

was closed, and the current produced by the cell was registered. After the cell had operated for several hours, the circuit was disconnected, the thimble, A (anodic compartment, Fig. 1), removed from C,

and the furnace cooled down. The salts of the anodic and cathodic compartments were separately dissolved in water and the solutions were analyzed as to their content of acid and of base. Methyl orange was used as indicator.

For experiments with inert gas atmospheres, such as hydrogen, nitrogen, and helium, the air was first pumped out of the tube (Fig. 2) and then the commercially pure inert gas was admitted. Moisture was removed from all of the gases, but the traces of residual oxygen were removed only from the hydrogen by means of a catalyst.

RESULTS

Electromotive force of the cell.—Measurements of the potential difference (emf) of the cell Ti/molten KCl/Pt were made in air and continued until this difference became approximately constant. Then the temperature was changed in order to establish the relation between the emf and the temperature. Some of the runs are listed in Table I. The table shows that the cell displays an emf of about 1.48 v at 900°C . The potential fluctuated during all of the experiments, but finally a fairly constant value (actually slowly decreasing) was established at a given temperature. There seems to be no relation between temperature and emf; usually the emf increased slowly from the beginning of the experiment up to a maximum value and then decreased slowly.

The values for the emf in a 50-50 mole per cent mixture of sodium and potassium chloride were approximately the same, reading about 1.48 v at 800°C . In pure sodium chloride they were somewhat lower, approaching 1.46 v at 950°C . All of these potential measurements represent open-circuit

TABLE I. Potential differences as shown by the cell Ti-Pt (open circuit) in molten KCl in presence of air

Time, min	Run No. I		Run No. III		Run No. V	
	Temp, $^\circ\text{C}$	Emf in v	Temp, $^\circ\text{C}$	Emf in v	Temp, $^\circ\text{C}$	Emf in v
0	900	—	1000	1.516	850	1.39
10	900	1.42	1000	1.518	—	—
20	900	1.45	1000	1.521	870	1.43
30	900	1.49	1000	1.520	—	—
40	900	1.48	950	1.527	900	1.44
50	920	1.48	950	1.524	—	—
60	900	1.48	950	1.522	—	—
70	900	1.49	950	1.521	—	—
80	900	1.49	950	1.517	—	—
100	—	—	950	1.515	910	1.48
160	—	—	950	1.484	900	1.47
180	—	—	850	1.496	—	—
200	—	—	850	1.468	—	—
220	—	—	850	1.453	900	1.48
270	—	—	850	1.441	—	—
280	—	—	800	1.403	900	1.45
325	—	—	800	1.301	—	—

TABLE II. Potential difference produced by the cell Ti/KCl, NaCl (molten)/Pt at 800°C in nitrogen and vacuum. Open-circuit values

Time, min	Gas	Emf in v
0	N ₂	0.42
5	N ₂	0.60
10	N ₂	0.58
15	N ₂	0.57
20	Vacuum	0.59
25	Vacuum	0.63
30	Vacuum	0.62
35	Vacuum	0.49
40	N ₂	0.55
50	N ₂	0.45

values. If a current was drawn from the cell, the emf dropped immediately (measured after opening the circuit), but started to increase slowly as long as the circuit was open and the temperature was constant, finally in several hours attaining the values mentioned above.

The emf as developed by the cell in an inert atmosphere or vacuum was much lower (Table II), and fluctuated between 0.45 and 0.60 v. Experiments in vacuum could not be continued for very long because the salt evaporated quickly from the crucible. Therefore, the remaining experiments were made using nitrogen under slight pressure (about 100 mm Hg); the cell developed approximately the same emf as listed in Table II. Replacing the nitrogen with helium or hydrogen gave essentially the same results. In the case of helium a greater emf was developed by the cell; evidently the helium contained some oxygen which was not removed prior to the experiments. The lowest emf of the cell, 0.35–0.50 v, was observed using hydrogen from which the oxygen had been removed. All of this indicates that the presence of air (oxygen) was necessary for the emf to appear. However, traces of water present in the salts can also cause an emf, as shown below.

Current produced by the cell.—As soon as the switch S (Fig. 1) of the Ti/molten salt/Pt cell was closed, such a strong current was developed in the first moments that it usually could not be measured by the instruments in the circuit. In a few seconds the current dropped abruptly, and slowly approached a fairly constant value, although it always fluctuated somewhat (Fig. 3). The sudden drop of the current is, of course, typical for a cell displaying polarization phenomena at the electrodes.

After the cell had been operating for a certain time, the circuit was opened and the furnace cooled. The salt from the anodic and cathodic compartments was removed, and separately dissolved in water. Qualitative tests showed that the solution obtained from the salt of the anodic compartment was strongly acidic, while that of the cathodic compartment was

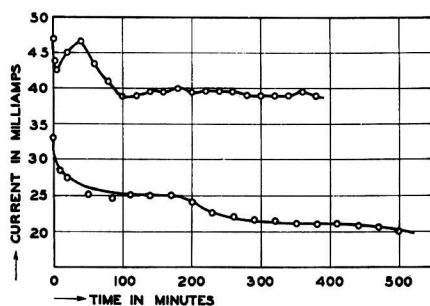


Fig. 3. Current developed by the cell Ti/molten NaCl, KCl/Pt vs. time at 800°C. Upper curve, Pt crucible as cathode; lower curve, a Pt sheet of 2 cm² as a cathode, electrode distance approximately 1 cm.

basic. A series of quantitative determinations was made in order to establish the amount of acid and base produced by the working cell.

The number of milliamperere minutes delivered by the cell were determined from graphs such as shown in Fig. 3, and from this were calculated the equivalents of metal going into solution in the anodic compartment as well as the deposition in the cathodic compartment. Because the electrolyte was usually a mixture of sodium and potassium chloride, only the equivalents or milliequivalents produced could be calculated (1608 ma min to correspond to one millieq.). The amount of acid and base produced by the working cell was determined by titration of the aqueous solutions of the salts of the separate compartments, and was compared with the calculated results based on the milliamperere minutes which flowed through the circuit. Results are summarized in Table III.

Table III shows clearly that acid and base are formed in appreciable amounts in the anodic and cathodic compartments, varying from 44 to 74% of the value as calculated from the current of the cell. The fact that the base and acid generated is appreciably lower than the theoretical value can be attributed to diffusion of reaction products through the porous alundum diaphragm so that partial neutralization occurred and, as a consequence, a smaller amount of base and acid was titrated. The fact that the amount of acid or base (Table III) is not equal is discussed later.

A series of qualitative experiments were made to determine the mechanism responsible for production of potential and current in the cell. It was found that the magnitude of the current obtained was dependent upon the presence of oxygen, similar to the results shown in Table II for emf of the open-circuit cell. At 800°C the cell delivered 35–40 ma; if the quartz tube containing the cell was evacuated, the current dropped to 0.27 ma or less. Upon ad-

TABLE III. Acid and base produced by the working Ti/molten salt/Pt cell in millieq.

Run No.	Salt	Millieq. calc. (from current)	Acid in millieq. anodic comp.	Base in millieq. cathodic comp.	Ratio of millieq. titrated to millieq. calculated
II	NaCl-KCl	1.18	0.37	0.51	0.51/1.18 = 0.44
Ia	NaCl-KCl	3.5	—	1.76	0.50
III	NaCl-KCl	7.35	3.45	5.05	5.05/7.35 = 0.69
IV	NaCl-KCl	9.55	5.24	6.0	6.0/9.55 = 0.63
6	KCl	4.65	1.91	2.81	2.81/4.65 = 0.60
7	KCl	2.29	1.12	1.68	1.68/2.29 = 0.74
9	NaCl	3.14	0.87	1.46	1.46/3.14 = 0.47

mission of air, again the current increased by a factor of 100 or more. This cycle could be repeated only a limited number of times, because the salt evaporated from the crucible when the vacuum was applied. However, alternate cycles of air and nitrogen gave, respectively, high and low currents for many repetitions. It seemed quite evident that oxygen acted as a depolarizer, maintaining by its presence the emf of the working cell. The action of other neutral gases was similar to that of nitrogen; they all decreased the current produced by the cell as soon as they displaced the air. However, in a hydrogen atmosphere the cell showed (at 800°C) a potential difference of only 0.35–0.50 v, but the current produced was somewhat higher than in nitrogen or vacuum; it fluctuated around 4 ma, but sometimes dropped to zero and became negative, which indicated that platinum went into solution. It may be that this behavior of titanium in a hydrogen atmosphere has some relation to the formation of titanium hydrides. The titanium was brittle after the experiments.

To check once more the depolarizing action of oxygen, it was introduced through a Vycor glass tube into the furnace (Fig. 1) so that the gas stream impinged on the platinum cathode. Immediately a current was observed with up to 4 times the value observed in air, indicating a pronounced depolarizing effect. Upon decreasing the oxygen stream, the current decreased also. However, it was necessary to prove whether the strong current observed on introducing oxygen was actually due to the depolarizing action at the cathode, or simply the result of stirring the electrolyte with the gas stream. If stirring caused the increase of current, then it could be expected that a nitrogen stream introduced near the cathode would also increase the strength of the current delivered by the cell. However, a nitrogen stream on the cathode caused a decrease of the current until it became even less than it was in air. Therefore, the effect of stirring of the bath was far below the effect caused by the chemical action of oxygen. In experiments with the nitrogen stream the

current did not drop to values as low as those observed in the experiments using inert gas atmospheres because of the oxygen still present. In the furnace (Fig. 1), the oxygen was only diluted by the nitrogen stream, but not completely displaced.

Many chemical reactions are influenced by water vapor even when only traces of vapor are present. To check this possibility, water vapor was introduced into the crucible of Fig. 1 through the tubing, D. The effect of the water vapor was quite impressive and resulted in currents which sometimes exceeded those generated in the presence of oxygen. Water vapor acted as a strong depolarizer.

In all experiments in which the current produced by the cell or the potential difference of the open cell was measured, it was impossible to say where the polarization or depolarization of the working cell occurred, whether on the anode or cathode, or on both electrodes simultaneously. Because of experimental difficulties and the lack of good reference electrodes (3) for temperatures close to 900°C, no attempts were made to measure the single potentials of the electrodes. However, an attempt was made to get an answer in an indirect way. For this purpose the titanium anode was completely encased in an alundum thimble by sealing its top with alundum cement and asbestos wool. Thus, the oxygen access to the anode was very limited. Oxygen, nitrogen, and steam were admitted alternately into the furnace (Fig. 1) near the cathode and the milliam-

TABLE IV. Depolarizing effect of oxygen and steam on the Ti/NaCl/Pt cell at 900°C

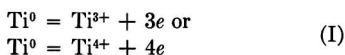
Ti anode was encased in a coarse grained alundum thimble. Time indicates the period after closing the circuit, and the moments at which the operations indicated are performed.

Time, min	Gas admitted	Current, ma
20	Air	85
25	N ₂ in	25
27	N ₂ off	85
30	O ₂ in	150
33	O ₂ off	120
39	N ₂ in	75
41	N ₂ off	110
45	O ₂ in	150
47	O ₂ off	120
49	N ₂ in	90
51	N ₂	80
53	N ₂ off	107
60	Steam in	170
61	Steam off	150 to 130
66	N ₂ in	100
68	N ₂ off	135
69	O ₂ in	150
70	O ₂ off	125
71	N ₂ in	90
76	Steam in and so on	150

meter readings were observed. The qualitative results obtained are shown in Table IV. It should be remembered that in such an experiment the current with admitted nitrogen never dropped to zero because the nitrogen only diluted the oxygen present in the furnace, as already mentioned. Nevertheless the experiment showed quite well the influence of the steam and oxygen. Table IV shows that a remarkably strong current can be drawn from the small cell for a period of several hours. The effect of oxygen, steam, or nitrogen on the current is decisive and appears immediately. For example, if the nitrogen stream is discontinued, the current increases immediately because of the action of the oxygen still present in the furnace. The same effects were produced with a titanium anode encased in a fine grained thimble, except that the current delivered by the cell was smaller because of the resistance of the alundum thimble walls. A comparison of these results with those obtained with an open anodic compartment shows that there was no difference in the general behavior of the cell, except that the current produced was more regular than with an open thimble (Fig. 3) and there was less titanium pyrosol in the closed thimble. Therefore, polarization and depolarization occurred mainly on the platinum cathode, and with a high speed.

DISCUSSION

There seems to be only one way to explain the behavior of the Ti/fused salt/Pt cell without contradictions. It has to be assumed that the titanium anode going into solution in the fused salt bath as Ti^{3+} or Ti^{4+} ions (in the presence of oxygen at the high temperature the oxidation of Ti^{3+} to Ti^{4+} would occur anyway) is the source of energy. Therefore, the anodic process is (4):



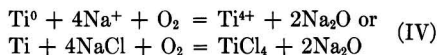
The electrons liberated pass into the platinum cathode, and attract the positive ions, which can only be the sodium or potassium ions. However, these ions can be discharged only in a limited amount to form a very thin alkali metal layer on the platinum cathode because the potential of the titanium is insufficient for a continuous reduction of alkali ions. Formation of such layers has been discussed previously (5). Under these conditions, only an insignificant fem is developed by the cell. The situation changes as soon as oxygen has access to the cathode; the electrons at the cathode can now be discharged at a fast rate by



because another cathodic energy delivering process is occurring:



Sodium peroxide may be also formed. The final process occurring in the cell during its operation is the sum of (I), (II), and (III):



Titanium displaces the sodium from the sodium chloride melt, and the sodium is oxidized by the oxygen of the air. Of course, a still better cathodic depolarizer is pure oxygen or water vapor; the latter reacts violently with the sodium with liberation of hydrogen. However, the presence of hydrogen could not be proved because of the high temperature; the platinum cathode would act as a catalyst in burning the hydrogen to water. Thus, oxygen or water vapor further the rate of reaction (II) and consequently increase the emf and the current of the cell. The reaction products, Na_2O and $TiCl_4$, dissolve in the salt of the cathodic and anodic compartments. No increase in weight of the platinum cathode after the experiments was observed, but it suffered from corrosion, especially in baths containing potassium chloride.

Thermodynamic calculations are difficult to apply, because the electrodes of the cell are not in equilibrium with the salt melt. However, very approximate estimations, taking into account the high concentration of the salt in the bath and the fact that at least in the beginning of the experiment the concentration of titanium ions is nearly zero, showed that reaction (IV) is thermodynamically possible.

Upon dissolution of the salt of the anodic and cathodic compartments separately in water, the titanium chloride hydrolyzes in water to give an acidic reaction, while the sodium oxide of the cathodic compartment gives the basic one. It follows from $Ti^{4+} + 4H_2O = Ti(OH)_4 + 4H^+$ and reactions (I) and (II) that the amounts of acid and base produced should be equal, regardless of whether Ti^{3+} or Ti^{4+} ions are formed. The lesser amount of hydrochloric acid actually obtained (Table III) can be explained by the partial evaporation of $TiCl_4$ during the experiment. Diffusion of the acidic and basic reaction products through the wall of the thimble during the runs and mutual neutralization after the dissolution in water explain the lesser amount of base or acid obtained as calculated from the current.

Encasing the anode did not influence the effects observed. So oxygen, steam, and nitrogen affect only the processes occurring on the cathode. No

attempt was made to determine the degree of anodic or cathodic polarization by direct determinations (3).

CONCLUSIONS

The experiments showed that in the presence of air, alkali oxides were produced on the cathode of a galvanic cell Ti/fused salt/ Pt by the emf of the titanium itself. If the same cell is now used for electrolysis by applying an external current and with titanium as the anode, alkali oxides will be formed on the cathode. This will happen even in the presence of titanium cations, because the formation of alkali oxides occurs at a lower potential than required for the discharge of Ti^{++} , as shown by the cell experiment. Hence no titanium can be deposited on the cathode because of this reason (other reasons are mentioned in the introduction).

Discharge of alkali cations on the cathode may also occur under an inert gas atmosphere, especially when the concentration of the titanium salt in the bath is low. Hence the discharging alkali ions will hamper deposition of titanium in the regular growth of the deposit, and formation of titanium powder will be favored. Furthermore, it may be that formation of titanium powder is also due to reduction of titanium ions by the electrolytic alkali metal formed (6). The possibility that titanium powder is formed through secondary reactions such as $Ti^{++} + 4Na = Ti^0 + 4Na^+$ is supported by observations on deposition of aluminum from cryolyte baths where, if the current is too strong (the voltage applied is too high, or the concentration of Al_2O_3 in the bath is too

low), alkali metals are discharged together with aluminum.

If the concentration of metallic titanium particles in the interface of the cathode during the electrolysis and the temperature is high enough, alloy formation with the cathode by direct contact of the particles may occur, as discussed in another article (7).

Of course, direct cathodic deposition of titanium is not excluded if the concentration of titanium salt in the bath is sufficiently high.

ACKNOWLEDGMENT

The authors are grateful to the Wright Air Development Center for continued support of this work and permission to publish the results obtained. Acknowledgment must be made to Dr. S. T. Shih for assistance on this particular phase of the project.

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

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The Extractive Metallurgy of Zirconium By the Electrolysis of Fused Salts

III. Expanded Scale Process Development of the Electrolytic Production of Zirconium from K_2ZrF_6

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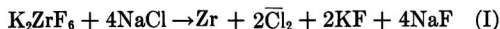
ABSTRACT

The electrolysis of K_2ZrF_6 in an electrolyte of NaCl to produce ductile zirconium metal has been expanded from the laboratory scale into a larger scale operation. An electrolytic cell capable of producing 3-4 lb of zirconium metal per run was designed and operated. Following successful operation of this unit, a cell capable of producing 30-40 lb of zirconium metal per run was used to evaluate the process on a scale 50 to 60 times the laboratory scale.

Electrolytic zirconium powder of high purity has been reproducibly obtained in good yields and at commercially acceptable current efficiencies. Upon consolidation, the metal shows fabricating properties comparable to those exhibited by Kroll sponge zirconium. The present larger electrolytic cell produces zirconium metal at a rate approaching that of the original commercial Kroll sponge producing reactors. Further expansion to larger scale operation should be entirely feasible.

INTRODUCTION

Two preceding papers (1, 2) on the extractive metallurgy of zirconium by the electrolysis of fused salts have discussed historical and theoretical aspects of this process, operational procedures, operational variables affecting the production of zirconium metal by the electrolysis of the double fluoride of zirconium, and the application of this process in producing high quality zirconium metal powder. The process can be summarized as being the electrolysis of fused potassium zirconium fluoride in molten sodium chloride in a purified argon atmosphere. The zirconium is deposited as dendritic crystalline metal in a matrix of salts from which it can be separated readily by water leaching. The over-all cell reaction is



In this paper, the expansion of the process from a laboratory unit capable of producing 200 g of zirconium per run to a cell in which 3-4 lb (1.3-1.8 kg) of zirconium metal per run can be made is described. This paper also describes the further expansion from this 3-4 lb cell, to a cell capable of producing 30-40 lb (13.5-18.0 kg) of zirconium metal per cathode at a rate of 4-6 lb/hr (1.3-2.7 kg/hr).

¹ Manuscript received July 6, 1954. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954 and is based on a portion of the work carried out by Horizons Incorporated for the New York Office of the Atomic Energy Commission under contract No. AT (30-1)-1144.

The zirconium metal produced in this expanded scale equipment has been evaluated by chemical analysis and by physical metallurgical procedures, and the results are presented.

FOUR POUND PRODUCING UNIT

Experimental Work

Equipment.—An electrolytic cell capable of producing 3-4 lb of zirconium in one 8-hour day by the electrolysis of K_2ZrF_6 in NaCl was designed and constructed at Horizons Incorporated. This cell represents approximately a tenfold increase in productive capacity over the laboratory cells previously described (2). It resembles the smaller cell in materials of construction and consists essentially of a graphite crucible and anode, a thermally insulated shell in which an inert atmosphere of argon can be maintained, and an operating head through which solid cathodes can be inserted into the molten bath. The cell is heated by a graphite resistance element. The cathode is comprised of a nickel rod to which a steel cathode is welded. The nickel rod is protected by a graphite sleeve within the cell and at the bath surface.

Normal operation consists of a charge melting period, a pre-electrolytic period, and the electrolysis. The cell and cathodic deposit are allowed to cool overnight to room temperature, and a 1-hr period at the beginning of the next cycle is used to remove the cathode and the crucible and to prepare for the subsequent run.

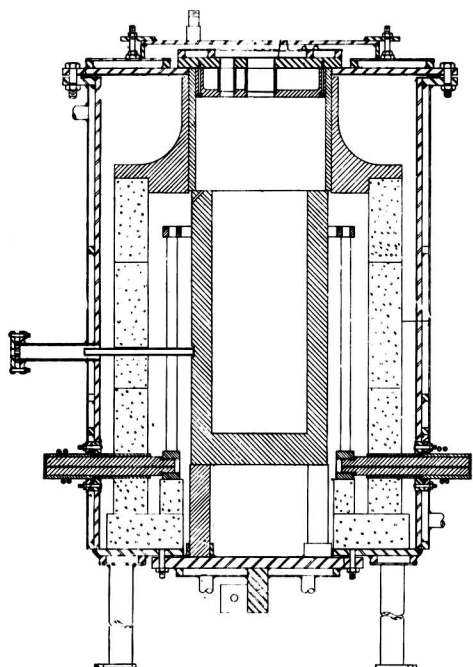





FIG. 1. Electrolytic cell.  graphite;  K-28 firebrick;  steel, nickel sheathed.

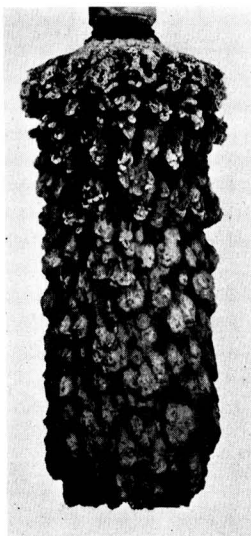


FIG. 2. Typical zirconium "carrot" on removal from electrolytic cell. $\frac{1}{5}$ normal size before reduction for publication.

Cell Operation

The electrolytic cell is cleaned and assembled as shown in Fig. 1, and the crucible is charged with granular sodium chloride. The salt is melted under

an argon atmosphere in about 2 hr with an a-c power input of about 24 kw. Dry potassium fluozirconate is then added to the molten sodium chloride through the charging hole and is rapidly melted. A normal starting charge is 10 lb of K_2ZrF_6 and 20 lb of NaCl. The bath temperature is controlled at 830°–850°C. A graphite cathode is immersed in the bath and a low voltage pre-electrolysis bath purification is performed. A small direct current starting at 1.5–1.8 v is passed through the bath for about 30 min, during which time the voltage increases to 2.8 v indicating removal of metallic impurities and water. At this voltage zirconium begins to deposit on the cathode and chlorine is evolved at the anode. The pre-electrolysis is continued for another 30 min at 2.8 to 3.1 v d.c. as a precautionary measure. A small amount of zirconium metal deposits out on the graphite rod. After this pre-electrolytic purification step, the bath is ready to be electrolyzed.

Upon removal of the pre-electrolytic cathode, a steel cathode is then immersed completely in the fused salt bath with a small d-c voltage impressed upon it. When the cathode reaches bath temperature (in about 5 min), the voltage is increased to 5 to 6 v d.c. to pass enough current to establish the initial current density at 300 to 400 amp/dm². When the cell polarizes, additional K_2ZrF_6 and NaCl are charged into the crucible. By this means, production of zirconium can be maintained at a consistently high rate.

When the predetermined number of ampere hours has been put through the electrolyte, the cathode is raised from the bath. The cathode is held above the bath, but in the argon atmosphere, and the entire unit is allowed to cool to room temperature.

Fig. 2 shows a typical cathode and cathode deposit after removal from the cell. Fig. 3 shows the deposit broken open to reveal the zirconium metal and the customary outer salt-metal layer.

Both crucibles and cathodes are reused; normal life for a crucible is 20 electrolyses or more and for a cathode, 100 runs. Cathodes are protected at the bath interface and in the chlorine atmosphere above the bath by graphite sleeves. These sleeves are replaced after each run.

Materials.—The cell, after any maintenance work or an extended shut-down, is made anhydrous by evacuation at 900°C at 50–100 μ . The K_2ZrF_6 is vacuum dried at 90°C and 150 μ for 2 hr before being charged into the cell. The sodium chloride used in this large unit is AR granular grade NaCl, supplied in 100-lb drums, and is used after drying in air at 120°C overnight. Melting the salts is carried out under a purified argon atmosphere.

In this work, three grades of potassium fluozirconate have been used: a C.P. grade K_2ZrF_6 , 99+ % in

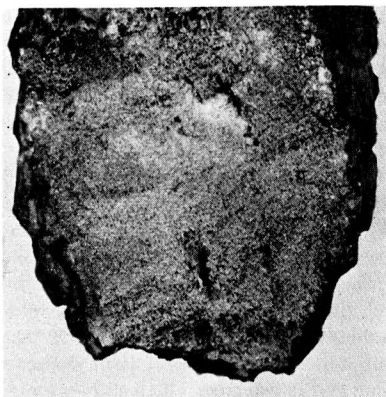


Fig. 3. Zirconium cathode "carrot" after breaking away part of the deposit showing the coarse zirconium powder, as deposited during electrolysis, and the outer salt layer.

purity, available commercially; double recrystallized K_2ZrF_6 , an anhydrous salt available commercially; and double recrystallized K_2ZrF_6 produced in the authors' laboratory from commercial grade K_2ZrF_6 .

Double recrystallized K_2ZrF_6 is required as the proper starting raw material for the production of low hardness zirconium metal. However, workable zirconium metal can be produced from commercial grade potassium zirconium fluoride. These conclusions are justified by the results of runs made in this unit. These results are shown in the tabulation of typical experimental runs given below.

Table I is a summary of a number of electrolyses in this larger scale unit. Three runs from each grade of K_2ZrF_6 used are summarized. All runs were made using a starting composition of 33% by weight of the fluozirconate and 67% by weight of sodium chloride.

In Table I, runs 1, 2, and 3 are typical of 29 electrolytic runs made with commercial grade K_2ZrF_6 . Zirconium produced with this material ranged in hardness from Rockwell A 57 to Rockwell

A 64 (Brinell 205 to 275). Current efficiencies are good, averaging 55–60%, but extremely wide variations were found in the chemical analysis, particularly in oxygen contents. The product is washed with more difficulty than that obtained from purer starting materials and, upon melting, fumes appreciably.

Per cent yield figures in runs 3–9 are lower than those obtained in strictly batch operations because of a change in operational procedure. Excess K_2ZrF_6 was added to the salt bath as the predetermined number of ampere hours were approached to keep the concentration of zirconium salt high. This cell ran for a predetermined number of ampere hours and the bath was not depleted of available zirconium.

Runs 4, 5, and 6 represent 17 runs made in the 4-lb cell using K_2ZrF_6 recrystallized in the laboratory and vacuum dried at 150°C. Consistently good quality zirconium, low in oxygen content, can be made with this salt as a starting material. The current efficiencies obtained in the electrolyses are somewhat lower, 45–55%, as are the over-all yields. The hardness of the zirconium is consistent at R_A 50–52 (Brinell 150–170). Oxygen contents of zirconium produced from this material range from 0.06 to 0.10%.

Runs 7, 8, and 9 represent 12 electrolytic experiments in which commercial anhydrous double recrystallized K_2ZrF_6 was used as the zirconium raw material. The electrolysis of this fluozirconate produces zirconium metal with Rockwell hardnesses from R_A 47 to R_A 51 (Brinell 145 to 170). Current efficiencies average 55–65%. The purity of the zirconium metal made in these experiments is very high. Oxygen contents range from 0.03 to 0.07% and carbon from 0.02 to 0.03%. Nitrogen contents, in nearly every run in this cell, average about 0.0035%.

Conditions of bath temperature and initial current

TABLE I. Summary of runs made in 3-4 lb zirconium cell

Run	Reference No.	Grade of K_2ZrF_6	Bath temp. °C	Current density amp/dm ²	Current efficiency	% yield	As-cast Rockwell hardness	Analysis		
								% O	% N	% C
1	92-69	Commercial CP	850	370	70	78.5	R_A 62	0.22	0.0027	0.037
2	92-77	Commercial CP	850	390	65	85.0	R_A 58	0.130	0.0031	0.051
3	92-103	Commercial CP	850	330	62	52.5	R_A 58	0.229	0.0028	0.056
4	92-121	Commercial CP Horizons recrystallized	850	325	47	59.0	R_A 52	0.080	—	0.017
5	92-123	Commercial CP Horizons recrystallized	850	340	45	44	R_A 52	0.088	0.0034	0.062
6	92-171	Commercial CP Horizons recrystallized	840	370	59	58	R_A 51	0.062	0.0099	0.028
7	92-173	Commercial double recrystallized	830	340	53	62	R_A 51	0.035	0.0008	0.024
8	92-177	Commercial double recrystallized	830	330	70	49	R_A 49	0.034	—	0.026
9	92-179	Commercial double recrystallized	835	370	61	56.5	R_A 48	0.042	—	0.025

TABLE II. *Typical screen analyses of electrolytic zirconium powder*
(USS Tyler Standard Sieves)

Run No.	+35	-35 +100	-100 +150	-150 +200	-200 +325	-325
92-96	0.4	30.2	24.0	18.2	20.2	7.0
92-103	1.0	15.8	12.2	20.4	34.2	16.4
92-123	7.8	17.8	12.4	17.2	27.8	17.0
92-177	0.2	20.2	14.8	26.4	25.6	12.8
92-179	0.2	31.4	14.4	29.8	18.0	6.2

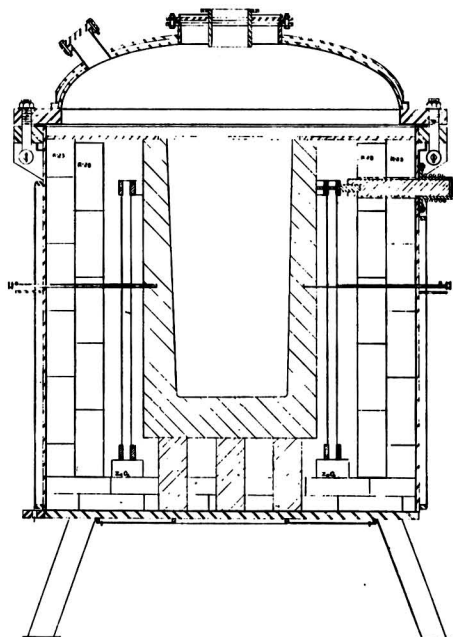




Fig. 4. Large scale electrolytic cell.  graphite;  K-28 firebrick;  steel, nickel sheathed.

density used in the 9 runs summarized in Table I have been established as the most desirable ones, not only in this larger scale equipment, but also in the small scale work previously reported (1, 2). In this 4-lb/run electrolytic cell, the electrolyses differ from the small scale operation in that additions of K_2ZrF_6 and NaCl were made during the electrolysis in order to avoid polarization and to keep the concentration of zirconium salts nearly constant in order to assure a supply of available zirconium. This cell is run, therefore, for a specified number of ampere hours. Hence, current efficiencies remain high, averaging about 55%, and are comparable to results obtained in the 200 gram cells with similar raw materials. However, the material yields are lower since this particular unit was operated as a batch unit and the bath was never run to exhaustion.

Yields reported in Table I should be considered in the light of this explanation.

Table II shows typical particle size distributions of the zirconium produced in this large laboratory electrolytic cell. No specific correlation has been made between particle size distribution and hardness for the zirconium powder, but, as a generalization, the coarser deposits tend to result in slightly softer metal upon melting. In some runs, the finer material has been found to result in harder ingots, but in other runs there has been no difference in the hardness of the consolidated metal. Coarse powder is preferable, however, since its recovery from the cathode deposit is easier and there is less loss in handling and in leaching. The metal is recovered by water leaching followed by air drying.

FORTY POUND PRODUCING UNIT

Experimental Work with 40-lb per Run Electrolytic Cell

Equipment.—A large scale electrolytic cell was designed (Fig. 4) to produce 30–40 lb of zirconium metal per run.² The design was based upon the laboratory electrolytic cell and the larger unit discussed above, with some modifications. Additional design features were incorporated, because of the increased physical size, in order to provide flexibility of operation, although it was not the intention to arrive at a prototype of a commercial cell.

This unit consists of a nickel-sheathed mild steel shell and is constructed on the interior much like the smaller units. It is completely water jacketed and is heated with a sectioned graphite heating element. The unit is insulated with refractory insulating brick on its sides and bottom. A machined graphite piece is both crucible and anode and can accommodate a 250–350 lb charge of molten salts. The cathode consists of jointed steel and graphite sections, the section upon which the zirconium metal is electrodeposited being mild steel. This section is threaded into a solid graphite rod which extends out of the cell through a nickel-sheathed operating head. The cell can carry up to 5000 amp direct current if desired. The unit operates in an argon atmosphere.

Cell operation.—Prior to its initial run, this unit was evacuated for eight hours at 900°C at a pressure of 35–125 μ . If any extended shut-down for maintenance or observation takes place between runs, the cell is again evacuated at a lower temperature before subsequent use. For these subsequent evacuations, a temperature of 200°C is adequate.

The crucible is brought up to 830–850°C operating temperature in about five hours, at which time the sodium chloride, about 170 lb, is charged. Analytical

² This cell was designed and built on ONR Contract No. Nonr-394 (01).

Reagent grade NaCl is used without predrying. Double recrystallized potassium zirconium fluoride, about 50 lb, is then added to the molten sodium chloride and is rapidly melted.

No pre-electrolysis is carried out in this large unit.

The steel cathode (including an additional 2-3 in. of graphite) is completely immersed in the fused salt bath with a small d-c voltage impressed upon it. The current is slowly increased until a current density of 260-300 amp/dm² is established on the cathode. When the bath polarizes, additional K₂ZrF₆ and NaCl are charged into the bath. Normally, a 50-50 mixture of K₂ZrF₆ and NaCl is used for the charge. By this means, the initial high production rate of zirconium metal can be maintained.

When a predetermined number of ampere hours has been passed through the electrolyte, the cathode is raised from the bath. The cathode is suspended above the bath, but in the argon atmosphere, and the entire unit is allowed to cool to room temperature.

Typical cathode deposits are shown in Fig. 5 and 6.

Some difficulty was experienced in this cell with crucible leakage and cathode breakage. Other graphite and nickel-clad parts appear to be satisfactory for reasonable service; that is, no gross attack has been observed in eight complete electrolytic cycles.

Table III is a summary of the runs made in this unit. As in the smaller unit, all runs were made using a starting composition of 33% by weight of the fluozirconate in the sodium chloride.

Metal recovery of electrolytic deposits.—Electrolytic deposits from the electrolysis of K₂ZrF₆ in fused sodium chloride average about 30% by weight of zirconium metal, the remainder being a mixture of soluble zirconium and sodium halides. The cold deposit is chipped away from the steel cathode by an air hammer and is then jaw crushed to about ¼ in. sized chunks. These lumps are then pulverized to about -80 mesh powder.

The crushed and pulverized cathode deposit is then leached in a continuous cone washer in which the metal is fluidized by an upward movement of water as the soluble salts are leached away and removed in the overflow. This unit represents, therefore, an approach to a continuous counter-current leaching operation.

When the zirconium metal is free of all soluble salts, it is removed from the water, filtered, and air dried.

PROPERTIES OF ELECTROLYTIC ZIRCONIUM

Physical Properties

The electrolytically deposited zirconium metal, in the form of dendritic crystals, is consolidated first by pressing into dense compacts 1 in. in diameter

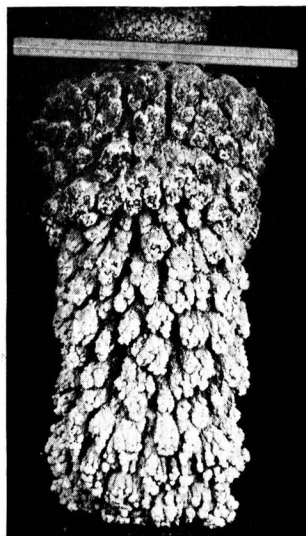


FIG. 5. Typical zirconium cathode deposit produced in the large scale electrolytic cell.

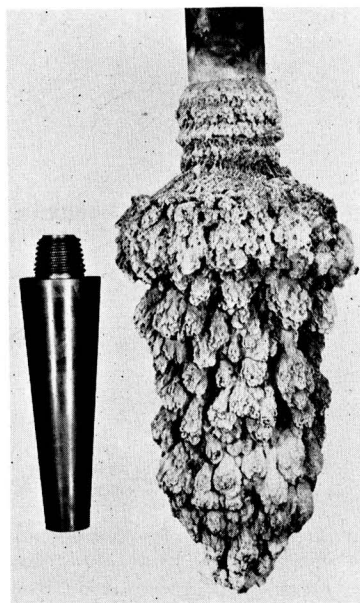


FIG. 6. Zirconium cathode deposit compared with typical mild steel cathode.

and ¼ in. to ⅜ in. in height. These compacts are then arc melted in a tungsten-arc, water-cooled, copper hearth furnace under a quarter of an atmosphere of argon. Fig. 7 shows typical zirconium metal dendritic crystals as produced in the large scale electrolytic cell. Fig. 8 shows uncompacted electrolytic zirconium, a compact of 20 grams of this powder, and an arc melted compact.

TABLE III. Summary of electrolytic runs made in large scale electrolytic cell

Run No.	Bath temp, °C	Initial current density, amp/dm ² on cathode	Current density amp/dm ² on anode	Current efficiency	Rate of production, lb Zr/hr of electrolysis	As-cast Rockwell hardness	Remarks
1	835	330	55	62	5.0	R _A 61	O ₂ = 0.320%; C = 0.015%
2	870	330	45	67	5.5	R _B 90	O ₂ = 0.108%; C = 0.045%
3	870	290	40	60	5.0	R _B 91	O ₂ = 0.061; C = 0.067%
4	820	330	45	65	5.3	R _B 87	
5	855	370	50	64	5.3	R _B 93	
6	840	270	37	53	3.8	R _B 88	

All runs made with starting concentration 33% K₂ZrF₆ by weight. Salt additions made during electrolysis, at bath polarizations.

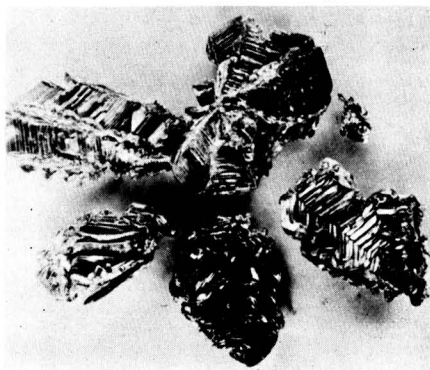


FIG. 7. Typical zirconium metal dendritic crystals

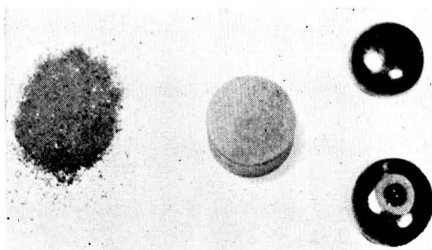


FIG. 8. Recovered zirconium powder, compacted zirconium powder, and small arc-melted zirconium ingots.

The arc furnace uses a tungsten electrode mounted in a water-cooled copper tube which is flexibly mounted in a copper head through a bellows assembly. The hearth is water-cooled copper, to take advantage of the fact that molten zirconium does not wet cold copper. The outer shell of this furnace is a cylindrical piece of Pyrex glass. Auxiliary equipment consists of an argon purification train of P₂O₅ and heated titanium sponge, a vacuum pump and cold trap, a manometer, and a 400 amp d-c Hobart

welder for the power source. It is similar to many which have been described in the literature.

Metal Evaluation

Rockwell hardnesses are taken on these arc melted pellets and this hardness becomes the primary means of product evaluation. Although hardnesses are customarily determined on the Rockwell B scale, a conversion from Rockwell A to Rockwell B scale was made since the hardness of zirconium alloys cannot always be made in the Rockwell B scale. This conversion between Rockwell A, Rockwell B, and Brinell is shown in Fig. 9.

Various melted pellets of 20–60 g and ingots of 100–150 g have been hot and cold reduced by rolling to determine the workability of the electrolytic zirconium. All of the metal produced can be hot worked to strip at 700°–800°C. Zirconium as-cast ingots or pellets, Rockwell B 85–92, can be cold rolled but are more successfully worked with successive anneals at 850°C (in air) after moderate

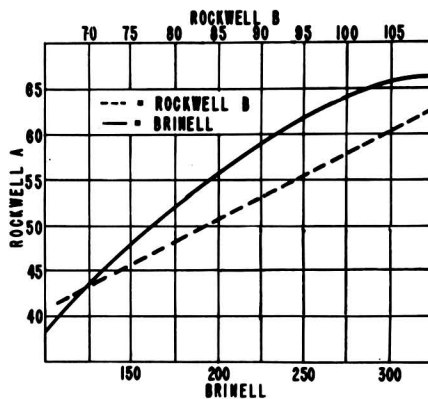


FIG. 9. Conversion from Rockwell "A" to Rockwell "B" and Brinell for zirconium.

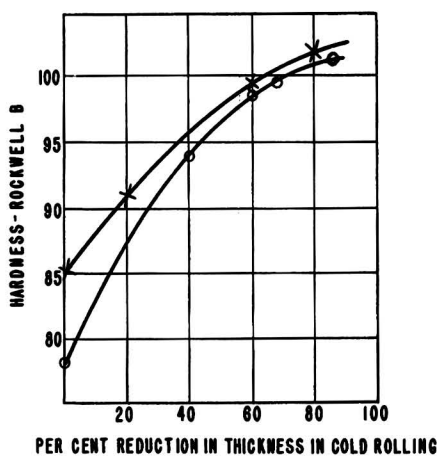


Fig. 10. Effect of cold rolling on the hardness of electrolytic zirconium.

TABLE IV. Spectrographic analyses of typical electrolytic zirconium powder and of rolled arc melted zirconium made from this powder

	Powder	Strip
Zr	Major	Major
Si	0.003	0.002
Fe	0.01	0.03
Al	0.01	0.007
Hf	1.5	1.5
Cu	0.0005*	0.0007
Ti	0.05	0.05
Ca	0.005*	0.005*
Mg	0.001*	0.001*
Mn	0.001*	0.001*
Pb	0.001*	0.001*
Mo	0.001*	0.001*
Ni	0.004	0.003
Cr	0.003	0.002
Sn	0.001*	0.001*
W	—	—

* Less than.

(20–40%) cold working. Fig. 10 illustrates typical hardness change with per cent reduction in thickness obtained in cold rolling of electrolytic zirconium. It can be seen that the hardness approaches R_B 100 during cold rolling before edge cracking, regardless of the initial as-cast hardness.

Spectrographic analyses of typical electrolytic zirconium powder as produced in the two electrolytic cells described above and of arc melted buttons made from this powder are given in Table IV. Typical oxygen analyses of such powder range from 0.06 to 0.09%, nitrogen from 0.003 to 0.009%, and carbons from 0.02 to 0.06% (see Table I).

CONCLUSIONS

The process development of the electrolysis of potassium fluozirconate in sodium chloride has been successfully expanded from the laboratory bench scale through a development-sized electrolytic cell capable of producing 3–4 lb to an electrolytic unit capable of producing 30–40 lb of zirconium metal per run. The process has been demonstrated to operate at commercially acceptable current efficiencies and yields and to produce good quality zirconium metal at a rate of about 4–6 lb/hr, which is equivalent to the production rate of the original Kroll sponge reactor. Results indicate that further expansion of the scale of operation will present no unsurmountable technical difficulties.

The zirconium metal, produced at this near-commercial rate of 4–6 lb/hr, has been evaluated, as as-cast metal, to have a hardness of Rockwell B 80 to Rockwell B 83 (Brinell Hardness Number 150 to 165), if recrystallized potassium zirconium fluoride is used as starting material. Such K_2ZrF_6 is readily available from commercial manufacturers.

Zirconium metal produced by the process, consolidated by arc melting, can be either hot or cold worked to sheet, foil, or wire. The oxygen content of this metal ranged from 0.06 to 0.09%; nitrogen averages 0.003%; and carbon 0.02 to 0.06%.

Comparison with Kroll Process

The operating schedule to produce 220 lb of zirconium by the Kroll magnesium reduction process (magnesium reacted with zirconium tetrachloride) is 41 hr and 30 min. The vacuum distillation of the yield of the reduction requires 42 hr and 10 min (3). Thus the 220 lb of zirconium are produced in 83 hr and 40 min. This is an over-all production rate of 2.6 lb of zirconium per hour for the Kroll process.

The electrolytic process time schedule, as obtained in the operation of its largest scale unit, is as follows for the production of 135 lb of zirconium: heat-up and melting of salt charge, 11 hr; electrolysis, 30 hr; metal recovery, 13 hr; total time, 54 hr. This is an over-all production rate of 2.5 lb of zirconium per hour, comparing favorably with the production rate obtained with the magnesium reduction process.

Another comparison between the two processes is possible. Excluding vacuum distillation time, the Kroll process requires 5.3 hr to produce 1 lb of zirconium. The electrolytic process produces zirconium at the rate of 3.3 lb of zirconium per hour, including cell heat-up time. However, more than one run can be made in a cell which is equipped with facilities for cathode removals without cooling-down

periods. If the initial 11-hr cell heat-up period is excluded, therefore, a production rate of 5.5 lb of zirconium per hour is achieved.

ACKNOWLEDGMENTS

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mission, to whom gratitude is expressed for permission to publish this paper.

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

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Conductances, Viscosities, and Densities of Solutions of Potassium Thiocyanate in Methanol at Temperatures within the Range 25° to -50°C¹

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ABSTRACT

Conductances, viscosities, and densities have been determined for solutions of potassium thiocyanate in methanol at nine temperatures within the range 25° to -50°C. Concentrations of potassium thiocyanate ranged from 4×10^{-4} to 1.75*N*. Good agreement exists between the observed behavior and the theoretical Onsager relationship for dilute solutions at all temperatures used in this study. The variation of conductances and viscosities of the more concentrated solutions is discussed with respect to both concentration and temperature.

INTRODUCTION

With the possible exception of certain ammoniacal systems, studies of electrolytic solutions at low temperatures are rather limited. The investigation summarized here represents part of a program intended to accumulate comprehensive data which may be useful in furthering the understanding of conducting nonaqueous solutions at low temperatures.

Potassium thiocyanate was selected for investigation because it is an inorganic salt which is not only quite soluble but also highly conducting in methanol, one of the few solvents for which dielectric constant data are available for low temperatures. According to the literature, the conductance of potassium thiocyanate in dilute methanol solutions has been investigated previously by Kreider and Jones (1) at 25° and 0°C (however, their data are uncorrected for the conductance of the solvent) and by Hartley and his associates (2) at 25°C. Inasmuch as little is known about this system except for conductance data for extremely dilute solutions at 25°C, it appeared to be quite worthwhile to investigate the conductance of potassium thiocyanate in methanol at lower temperatures and over a greater concentration range as well as to determine the corresponding viscosities of solutions in which the viscosity differs appreciably from that of the solvent.

EXPERIMENTAL

Absolute methanol was purified using the procedure described by Evers and Knox (3). Conductivities of the retained middle fractions were approximately 10^{-7} ohm⁻¹ cm⁻¹. Reagent grade potassium thiocyanate was rendered anhydrous by the

method of Kolthoff and Lingane (4) and used without further purification. Concentrated solutions were prepared by adding a weighed quantity of methanol to a known weight of potassium thiocyanate, whereas the dilute solutions were prepared by the weight dilution of stock solutions. Sufficient amounts of the concentrated solutions were prepared to permit separate portions of a solution to be used for measuring the conductance, viscosity, and density. Necessary buoyancy corrections were applied to all weights. Weight-based concentrations were converted to a volume basis through utilization of the proper density data. All transfers were made in a dry box.

A Jones bridge (manufactured by the Leeds and Northrup Company) was used to measure resistances of the solutions contained in the conductance cells. For larger resistances, 30,000 ohms of the bridge resistance was shunted in parallel with the cell and the series cell resistance was computed from the measured parallel resistance. The constants (ranging from 0.2502 to 31.99 cm⁻¹) of the Jones and Bollinger cells (5) having electrodes platinized by the standard procedure (6) were determined using standard 0.01 demal aqueous potassium chloride solutions according to the method of Jones and Bradshaw (7) or by intercomparison of resistances with cells having known constants. Resistances of solutions measured at 500, 1000, and 2000 cycles were found to have no significant frequency dependence. Conductance of the potassium thiocyanate was obtained by subtracting the conductance of the solvent from that of the solution. In no case did the solvent correction exceed 2%.

Two size-50 Ostwald-Cannon-Fenske viscometers were used in measuring efflux times of the solutions. Calibrations of the viscometers were based on the

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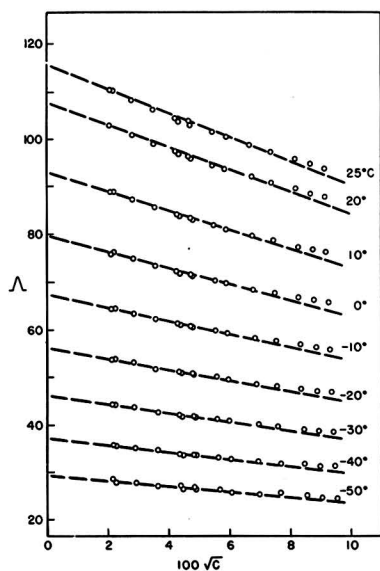


FIG. 1. Kohlrusch plots for potassium thiocyanate at low concentrations in methanol.

TABLE I. Some physical properties of methanol

°C	Density (g/ml)	Viscosity (millipoises)	Dielectric constant (11, 12)
25	0.7866	5.42	32.6
20	0.7916	5.81	33.7
10	0.8010	6.76	35.6
0	0.8102	7.94	37.5
-10	0.8200	9.41	39.6
-20	0.8296	11.3	41.8
-30	0.8390	13.8	44.0
-40	0.8485	17.2	46.2
-50	0.8580	21.9	48.5

TABLE II. Test of Onsager's equation for solutions of potassium thiocyanate in methanol at temperatures within the range 25° to -50°C

°C	Limiting equivalent conductance	Observed slope (S_g)	Theoretical slope (S_T)	$\frac{(S_g - S_T)}{S_T} \times 100$
25	115.7	-259	-253	3
20	108.0	-240	-233	3
10	93.3	-205	-197	4
0	79.8	-171	-166	3
-10	67.4	-139	-138	1
-20	56.0	-110	-110	0
-30	46.0	-91	-92	-1
-40	37.0	-72	-73	-1
-50	29.3	-58	-57	2

efflux times of water and two National Bureau of Standards viscosity oils (D-8 and H-8) at 20°C. Viscometer constants at temperatures other than the calibration temperature were calculated using

the equation introduced by Cannon and Fenske (8). Calibrated timers reading directly to 0.2 sec were employed to measure efflux times of the solutions through the viscometers. The viscometer arms were vented to the atmosphere through drying tubes containing anhydrous calcium chloride and Ascarite. Appropriate kinetic energy corrections were applied in the calculation of viscosities. All viscosity data are referred to the viscosity of water, 1.002 centipoise at 20°C (9).

Densities of the solutions were determined using two Pyrex pycnometers of 22.3 and 22.4 ml capacities. Each pycnometer consisted of a spherical bulb to which was sealed a small-bore graduated stem closed at the other end with a ground-glass cap. Calibrations of the pycnometers were made at 20°C using distilled water. Applying the necessary corrections for cubical contraction of Pyrex glass, the pycnometer volumes were calculated at ten-degree intervals over the temperature range from 20° to -50°C.

All measurements were carried out in a manually controlled thermostat consisting of a five-gallon Dewar flask containing impure ethanol cooled by adding powdered dry ice. Vigorous agitation of the bath liquid was obtained through the use of a mechanical stirrer having three sets of propellers. Temperatures in all cases were observed by the use of alcohol-filled thermometers which were periodically compared with two thermometers calibrated by the National Bureau of Standards. Emergent stem corrections were unnecessary inasmuch as thermometers were totally immersed in the bath liquid. Measurements were made at 25°, 20°, 10°, 0°, -10°, -20°, -30°, -40°, and -50°C. In each case the temperature could be controlled well within 0.2°.

RESULTS AND DISCUSSION

Plots of the equivalent conductance, Λ , of potassium thiocyanate in methanol at various temperatures against the square root of concentration are shown in Fig. 1. The dashed line in each case represents the theoretical behavior predicted by the Onsager equation (10) which may be written as follows for a uni-univalent electrolyte:

$$\Lambda = \Lambda_0 - [A + B]\sqrt{C}$$

where

$$A = \frac{82.42}{(DT)^{1/2}\eta}$$

$$B = \frac{8.203 \times 10^5}{(DT)^{3/2}}$$

in which D and η are the dielectric constant and viscosity of the solvent, respectively.

TABLE III. Limiting equivalent conductances and dissociation constants determined by Shedlovsky method and conductance-viscosity products for potassium thiocyanate in methanol

	Λ_0	K	$\Lambda_0\eta$
°C			
25	115.7	0.09	0.627
20	107.8	0.09	0.626
10	93.1	0.09	0.629
0	79.7	0.10	0.633
-10	67.4	0.13	0.634
-20	56.0	0.11	0.633
-30	46.0	0.20	0.635
-40	36.9	0.59	0.633
-50	29.2	0.35	0.638

Viscosity and dielectric constant data used in the calculation of the theoretical slope, $-[A + B\Lambda_0]$, may be found in Table I. A summary of the limiting equivalent conductances, obtained by extrapolation, and the observed and theoretical limiting slopes is given in Table II. It may be noted that good agreement exists between observed and theoretical slopes; however, the observed slope generally is slightly more negative than the theoretical slope which may be evidence of incomplete dissociation of the solute. The equivalent conductance data were analyzed, therefore, by the Shedlovsky method (13) which permits simultaneous evaluation of the limiting equivalent conductance and the dissociation constant. The resulting data obtained from the intercepts, evaluated by the method of least squares, and slopes of plots of $S\Lambda$ vs. $Cf_{\pm}^2S^2\Lambda^2$ may be found in Table III. The dissociation constants indicate that potassium thiocyanate is very highly dissociated in methanol and that its dissociation becomes even more pronounced at lower temperatures. The corresponding Λ_0 values listed in Tables II and III agree within experimental and extrapolation errors. The limiting equivalent conductance value of 115.7 $\text{ohm}^{-1} \text{cm}^2$ for potassium thiocyanate in methanol at 25°C is approximately 1% greater than that reported by Hartley and his associates (2).

Fig. 2 shows that a plot of the logarithm of the limiting equivalent conductance of potassium thiocyanate in methanol vs. the reciprocal of the absolute temperature is linear over the temperature range studied. Consequently, for the system under consideration it is possible to regard conductance as a rate process (14) in which case the relation between Λ_0 and T can be written in the form, $\Lambda_0 = A \exp(-E/RT)$, where A and E are constants, E being the energy of activation for the process of ionic transport through the solution. E amounts to 2.42 kcal for potassium thiocyanate in methanol, whereas it is approximately 3.60 kcal for most normal electrolytes in water. Fig. 2 also shows that the logarithm of the viscosity of methanol vs. $1/T$

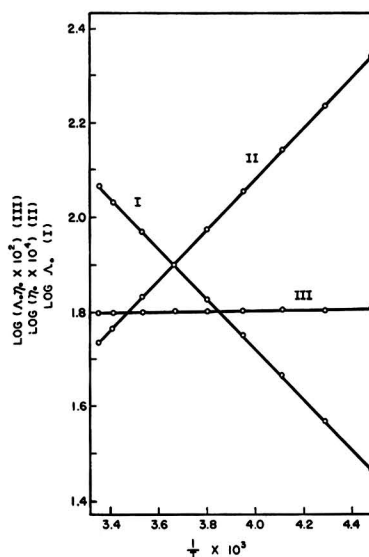


FIG. 2. Logarithms of the limiting equivalent conductance, viscosity of the solvent, and the product of these values, as functions of the reciprocal of the absolute temperature.

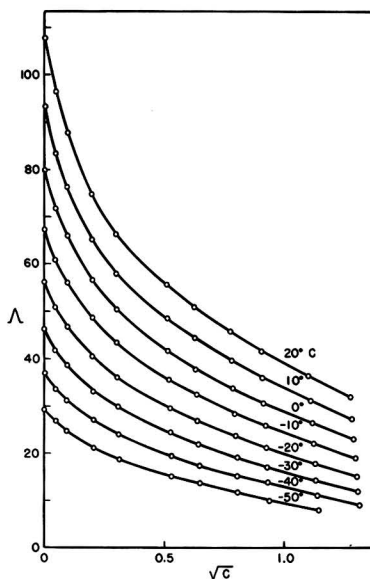


FIG. 3. Kohlrausch plots extending to higher concentrations of potassium thiocyanate in methanol.

is linear, indicating that the relation between η_0 and T may be written in a similar form, $\eta_0 = B \exp(E'/RT)$, where B and E' are constants, E' being the activation energy of viscous flow. For methanol E' equals 2.47 kcal. Combining the logarithmic expressions of the two equations given above, the expression $\log_{10}(\Lambda_0\eta_0) = \text{constant} +$

$(E' - E)/2.303 R 1/T$ may be obtained. Hence, a plot of $\log (\Delta_0 \eta_0)$ vs. $1/T$ should be linear, and the slope should be a function of the difference of the activation energies of the conductance and viscous flow processes. A combined plot of this nature for potassium thiocyanate in methanol may be seen in Fig. 2. If the activation energies were equal, the

equation would reduce to Walden's rule, $\Delta_0 \eta_0 = \text{constant}$. Quite aside from any question related to mechanistic processes, however, equality of the so-called activation energies means simply that the positive conductance temperature coefficient is approximately equal to the negative viscosity temperature coefficient. Hence, the product of the limiting

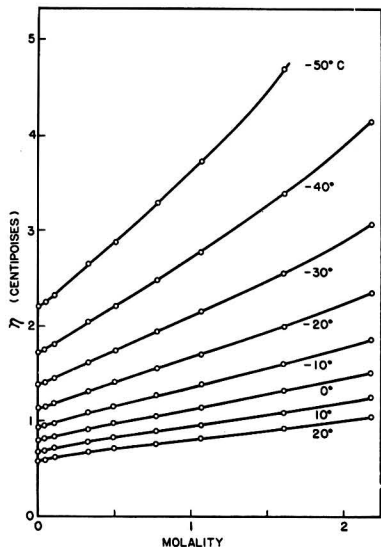


FIG. 4. Concentration dependence of the viscosity of solutions of potassium thiocyanate in methanol.

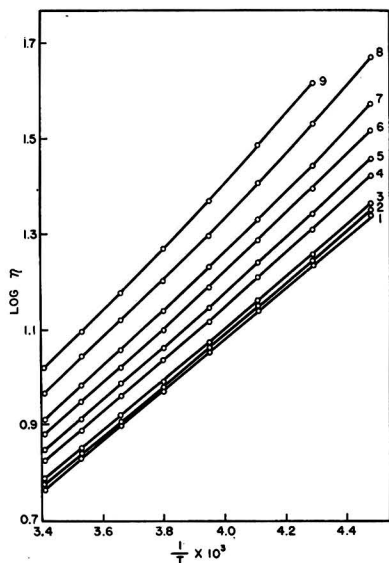


FIG. 5. Temperature dependence of the logarithm of the viscosity of solutions of potassium thiocyanate in methanol. (1) solvent; (2) 0.0482*M*; (3) 0.111*M*; (4) 0.329*M*; (5) 0.498*M*; (6) 0.777*M*; (7) 1.065*M*; (8) 1.604*M*; (9) 2.183*M*.

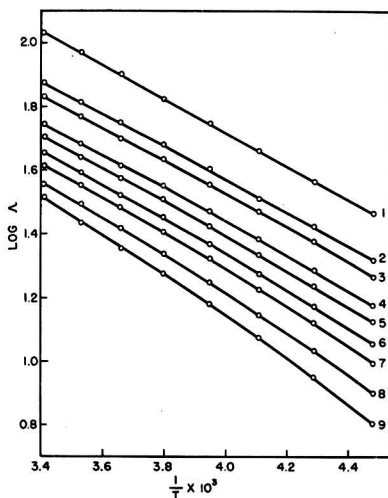


FIG. 6. Temperature dependence of the logarithm of the equivalent conductance of potassium thiocyanate in methanol. (1) Λ_0 values; (2) 0.0482*M*; (3) 0.111*M*; (4) 0.329*M*; (5) 0.498*M*; (6) 0.777*M*; (7) 1.065*M*; (8) 1.604*M*; (9) 2.183*M*.

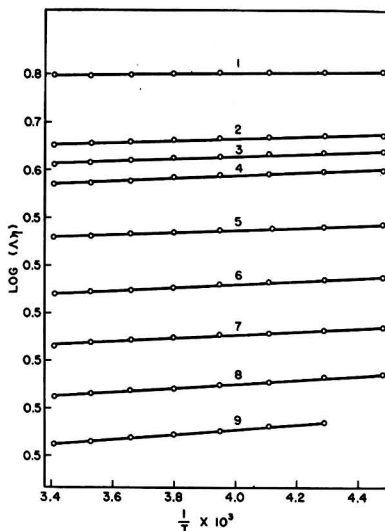


FIG. 7. Logarithm of the product of the equivalent conductance and the viscosity of the solutions as a function of the reciprocal of the absolute temperature. (1) 0.00*M*; (2) 0.048*M*; (3) 0.111*M*; (4) 0.329*M*; (5) 0.498*M*; (6) 0.777*M*; (7) 1.065*M*; (8) 1.604*M*; (9) 2.183*M*.

equivalent conductance and the viscosity of the solvent should be approximately constant. The values of this product for potassium thiocyanate in methanol at various temperatures are listed in Table III.

Fig. 3 shows Kohlrausch plots for potassium thiocyanate in methanol covering the entire concentration range studied. Plots for the various temperatures are similar in shape and differ principally only in the magnitude of displacement along the ordinate. The variation of viscosity with molality for solutions of potassium thiocyanate in methanol at various temperatures is shown in Fig. 4. Curvature of the plots becomes more pronounced at lower temperatures. Density plots have not been included because the following equation describes within 1 mg/ml the densities of this system within the temperature range from 20° to -50°C for concentrations up to 2.183*m*:

$$d = 0.7916 - (0.000943 - 0.000044m)(t - 20) + 0.530m - 0.00095m^3$$

where *d* = density in g/ml, *m* = molality, and *t* = temperature in °C.

Plots of the logarithm of the viscosity vs. 1/*T* for various molal concentrations of potassium thiocyanate in methanol appear in Fig. 5. It may be observed that the graphs become more curved as molality increases. Fig. 6 presents corresponding plots of the equivalent conductance vs. 1/*T* for the same molal concentrations. If plots for various molar concentrations were constructed, the over-all picture would not be changed appreciably. Nevertheless, these graphs become more curved with increasing molality in the same manner as the viscosity plots in Fig. 5. The logarithm of the conductance-viscosity product, at the same molal concentrations, as a function of the reciprocal of the absolute temperature is shown in Fig. 7. In this figure the ordinate

value has been displaced 0.1 logarithm unit for each of the five most concentrated solutions to prevent superposition of the curves. The plots are linear and have slopes which increase with increasing molality. Whether the linearity results from fortuitous cancelling effects or depends upon a constant difference in the activation energies of conductance and viscous flow or other factors is unknown. However, for the system potassium thiocyanate in methanol, the conductance-viscosity product is not a constant over the temperature range 20° to -50°C, but can be expressed empirically by an equation of the form, $\Delta\eta = A \exp(B/RT)$, where *A* and *B* are constants characteristic of a particular molal concentration.

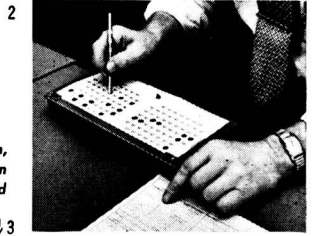
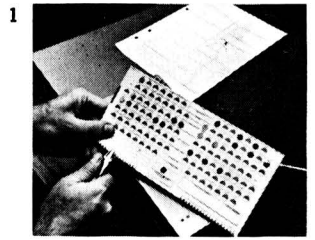
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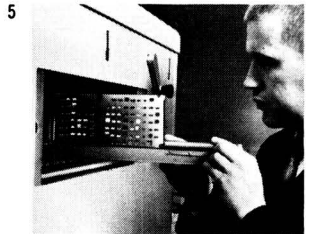
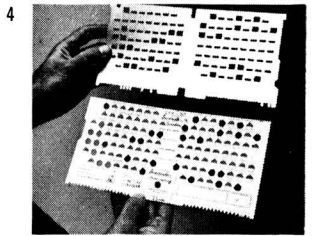


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Cincinnati Meeting, May 1 to 5, 1955



Skyline of Cincinnati taken from northern Kentucky shores

The Spring Meeting of the Society will be held May 1 to 5 at the Sheraton-Gibson Hotel in Cincinnati, Ohio. Sessions of the Electric Insulation, Electronics, Electrothermics and Metallurgy, Industrial Electrolytic, and Theoretical Electrochemistry Divisions will be featured.

Reservations

The Sheraton-Gibson, Cincinnati's leading convention hotel, is located at Fourth and Walnut Streets in the heart of the downtown area. Fronting on historic Fountain Square with the famous Tyler-Davison Fountain, it is most convenient to business, shopping, and theatrical districts and will be the location for all general and division meetings.

All rooms are equipped with radio, tub or shower-bath, and most rooms have air-conditioning and TV sets.

Requests for room reservations should be sent to Mark Schmidt, General Manager, Sheraton-Gibson Hotel, Cincinnati 1, Ohio, stating name and address, date and time of arrival and

departure, and mentioning The Electrochemical Society. Hotel reservation cards will be mailed with the Program Booklet late in March.

Technical sessions will be held on the Mezzanine Floor, the Ball Room Floor, and the Roof Garden of the hotel.

General Functions

On Monday, May 2, an informal evening get-together and entertainment has been planned. Cocktails will be served at 6:30 P.M. in the Foyer of the Roof Garden. Buffet Supper with floor show and entertainment will follow.

The Electrochemical Society Luncheon and Annual Meeting will be held Tuesday, May 3, at 12:30 P.M. in the Roof Garden. The Annual Meeting will be presided over by the President.

The President's reception will be held at 6:30 P.M., Tuesday, in the Foyer of the Roof Garden, followed by cocktails and dinner in the Roof Garden.

A Section Q meeting and informal get-together with a Selling Bar and snacks will be held in the Victory Room, Lower Lobby, Wednesday evening.

Plant Trips

The following plant trips have been planned:

Tuesday afternoon—An inspection of the main plant of the Baldwin Piano Company, Gilbert Avenue at Eden Park entrance, has been arranged. This trip will include inspection of the plant and processes used in the manufacture of pianos and electronic musical instruments.

Wednesday afternoon—An inspection of the new Walter C. Beekjord Electric Generating Station of the Cincinnati Gas & Electric Company on the Ohio River near New Richmond, Ohio, has been arranged. This station has a capacity of 325,000 kw, and its latest generating and steam units have been placed in service within the past three months. This modern, high pressure steam station with complete river fuel deliveries, automatic handling and control equipment is worth seeing for its educational value as well as the scenic ride up the Ohio River.

Thursday afternoon—An inspection trip through the Public Health Center



Taft Museum, home of President William Howard Taft

of the Federal Government on Columbia Parkway has been arranged.

Ladies' Program

A complete Ladies' Program has been arranged by an active committee to encourage participation of the ladies in the Cincinnati convention. Ladies' Headquarters will be maintained at the Hotel throughout the meeting, and all ladies are requested to visit this headquarters and register for the program which has been arranged for their entertainment and information. In addition to sight-seeing, shopping, and individual amusement, the Ladies' Program will include the following features:

Monday morning—A get-acquainted meeting with coffee and doughnuts.

Monday afternoon—A style show, with monologue by Miss Bernice Foley. Miss Foley is a nationally recognized authority on style and charm, and will bring her knowledge of these arts to the ladies. The style show will be followed by tea.

Tuesday—A trip has been arranged to the new Robert A. Taft Engineering Center operated by the U. S. Department of Health, Education, and Welfare. Work at the Center includes air pollution control, water pollution control, radiological experimentation, and environmental health investigations and engineering. Luncheon will be served at the Center.

Wednesday—The ladies are invited to participate in a Cincinnati Motorama, leaving the Sheraton-Gibson Hotel at 10:30 A.M. This trip will provide thumbnail views and sketches of interesting points in and around Cincinnati. It will be followed by luncheon at one of the finest restaurants on the famous Dixie Highway across the river in Kentucky.

Thursday—Held open for shopping and departure of the ladies who are invited to make the Ladies' Headquarters a get-together place for information and advice as to places to visit and things to see and buy.

In addition to the above special arrangements, all of the ladies are invited to participate in the general functions of the meeting, including the Monday evening Buffet Supper, cocktails, and floor show, and the Tuesday evening reception and dinner.

Cincinnati—Seven Hilltops

Built upon seven hills, Cincinnati is one of America's most picturesque big cities. Visitors appreciate, perhaps more than its natives, panoramic views from hilltop parks and streets, stern-wheelers churning the Ohio River, and 1001 other sights around the town. The following sketch is intended for those who may be visiting the Queen City for the first time.

Transportation-wise, Cincinnati might be called the crossroads of the nation. Located literally in the center of the U.S. industrial world, it is the nearest large industrial city to the center of population. With seven railroads, five airlines, and uncountable river craft, it can justifiably point with pride to its new greater Cincinnati Airport, its modern railroad terminal, and one of the great river harbors of the Ohio where leave the only packet boats left on the Ohio River.

The Cincinnati Union Terminal is considered the most beautiful railroad station in the nation. Its huge rotunda dominates a well landscaped approach and its interior is decorated with large murals depicting the various major industries of the city. The area immediately surrounding the terminal is

gradually being redeveloped with low-rent housing projects, another step in the development of Cincinnati's Master Plan. This long-range plan, when completed, will link the downtown area with the suburbs by means of a network of expressways and will have redeveloped all blighted and unsightly areas within the city limits.

Those to whom industry is of primary concern will find that variety is the spice of Cincinnati's manufacturing life. Cincinnati Milling Machine Company, Procter & Gamble, and U. S. Playing Card Company are the largest manufacturers of their respective products in the world. The Gas Turbine Division of General Electric, world's largest producer of jet engines, is located in Evendale, just beyond the city limits of Cincinnati. This gigantic plant is popularly referred to as "Jet Center, U. S. A." Public Utilities have kept pace with the city's growth. The Cincinnati and Suburban Bell Telephone Company was one of the first companies to be completely dial operated. The Cincinnati Gas & Electric Company, in addition to erecting new office facilities, has placed two 100,000-kw generating units in operation at its new Walter C. Beckjord Station at New Richmond. A new 125,000-kw unit is nearing completion at this time and another 125,000-kw unit is contemplated for construction in the near future. The Atomic Energy Commission has recently completed work on its uranium ore refining plant at Fernauld, Ohio, several miles from Cincinnati. The over-all cost of this plant ran in excess of 450 million dollars.

For those visitors interested in things cultural and educational, we suggest visiting the Art Museum located in beautiful Eden Park; Taft Museum, home of President William Howard Taft, located near Lytle Park; the new ultramodern Public Library in the heart of downtown Cincinnati; the Zoological Gardens, where each year is held the Summer Opera with Metropolitan stars; the Botanical Gardens, also located in Eden Park; Rookwood Pottery in Mt. Adams, world famous for its pottery and porcelains; and the University of Cincinnati, one of the largest municipally owned institutions in the world and originator of the now famous cooperative plan of technological education in its Engineering, Business, and Applied Arts Colleges. This plan has since been adopted by many colleges and universities throughout the United States.

For epicures and gourmets, Cincinnati

nati recommends its many beautiful hotel dining rooms, as well as its Italian, French, and Chinese restaurants. And for the sportsmen, we offer Crosley Field, home of the National League Cincinnati Reds, and the Cincinnati Gardens, one of the nation's largest indoor sports arenas, completed in 1948. A complete view of the arena, unhampered by interior columns, can be had from any one of its 12,000 permanent seats. Ice shows, ice hockey, basketball, public ice skating, and many other sporting events take place throughout the year in this huge arena.

Generally speaking, industry and culture of every type and description are represented in the Cincinnati metropolitan area.

NEWS ITEMS

New Sustaining Members

Bart Manufacturing Company, Belleville, N. J., and Radio Corporation of America, RCA Victor Division, Harrison, N. J., recently became Sustaining Members of the Society.

Weyerhaeuser Timber Co. to Build Chlorine Plant

The Pulp Division of Weyerhaeuser Timber Company of Tacoma, Wash., plans the erection of an electrolytic cell plant at Longview, Wash. The pulp mills at Longview and Everett, Wash., will consume the entire production of chlorine and caustic soda. The rated capacity of the new installation is about 100 tons of chlorine per day.

R. B. MacMullin Associates of Niagara Falls, N. Y., prepared the preliminary surveys and have been retained to design the plant.

The construction schedule calls for start-up in the fall of 1956. No costs have been announced.

Carborundum Co. Establishes New Operating Unit

The Carborundum Company has established a new operating unit, the "Electro Minerals Division," to manufacture and sell silicon carbide and fused alumina crudes, abrasive grain, and related electric furnace products in the United States. Mr. Joseph S. Imirie, formerly assistant to the president, will be general manager of the new division. The creation of the Electro Minerals

Division was a step in the company's policy to decentralize and specialize along basic product lines.

The large Bonded Products and Grain Division in Niagara Falls, N. Y., which formerly encompassed the responsibilities now allocated to the Electro Minerals Division, will be designated "The Bonded Abrasives Division" and will specialize in the manufacture and sale of grinding wheels, sharpening stones, and other bonded abrasives, which include over 30,000 standard products each year.

The Electro Minerals Division was established to provide effective quality control for the crude and grain products which are vital not only to Carborundum but to the abrasives industry at large. It also establishes a single responsibility and organizational medium to strengthen the conventional uses of silicon carbide and fused alumina in the abrasives, super refractories, and electrical industries, and expand their use into new markets. The Electro Minerals Division is also intended to facilitate the production and sale of other electric furnace products now emerging from the research and development stages.

The facilities and personnel included in the new division are the silicon carbide furnace plant, fused alumina furnace plant, abrasive grain and powder processing facilities, and the storage and auxiliary equipment at Niagara Falls, N. Y., the silicon carbide furnace and crushing plant in Vancouver, Wash., together with all the company's employees at these installations.

G.E. Light Amplifier Demonstrated

A long-sought scientific goal—direct amplification of light without use of electronic tubes—was demonstrated recently by scientists from the General Electric Research Laboratory, Schenectady, N. Y.

"Discovery of this light amplifier may be the clue to achieving 'picture-on-the-wall' television screens," according to Dr. C. G. Suits, G.E. vice-president and director of research.

Although the new scientific phenomenon may have great importance in the future of television, x-ray fluoroscopy, photography, "seeing-in-the-dark" devices, and other developments involving reproduction of picture images, Dr. Suits emphasized that no immediate application should be anticipated. He said that the importance of the demonstra-

tion lies in the new scientific knowledge involved in achieving light amplification for the first time in a simple phosphor film. "G.E.'s experimental screens, made of a special phosphor to which an electric field is applied, have given off ten times as much light as that projected on them."

In the demonstration, scientists increased the brightness of a projected photograph by passing an electric current through a special phosphor cell used as the viewing screen. Dr. F. E. Williams, head of light generation studies at the laboratory, said the light-amplifying phosphor was created by D. A. Cusano, young G.E. scientist who conducted the demonstration.

An ordinary lantern-slide projector was employed, and the picture was a regular photo slide. The small screen reflected a yellowish image when an ultraviolet light source was used in the projector. As the voltage on the screen was increased, the picture became brighter in the manner usually achieved either by increasing the intensity of the projector light or by opening the lens aperture. Neither the light nor the lens was altered, however, and the picture—which at first was barely visible—became many times brighter and clearer. During the over-all brightening of the projected picture, the contrast remained virtually unchanged, thus demonstrating proportional amplification.

Dr. Suits pointed out that the demonstration was of a new scientific phenomenon, but because of the small size of the screen (about four inches across) and the limitations in the type of light that can now be amplified, no immediate applications for picture projection screens should be anticipated.

G.M. Fellowship in Electrochemistry

Wayne University has announced the establishment of the General Motors Fellowship in Electrochemistry by the Research Laboratories Division of the General Motors Corporation. The purpose of the fellowship is to allow qualified students to further their graduate training in the field of electrochemistry. Anyone desiring further information may write to Dr. George H. Coleman, Chairman, Department of Chemistry, Wayne University, Detroit 1, Michigan.

During the past year the fellowships were held by John J. Hoekstra and Bienvenido C. Sison, Jr., whose research was directed by Dr. Dan Trivich, Associate Professor of Chemistry.

Bylaws of The Electrochemical Society, Inc.

(As Approved at the Board of Directors' Meeting, January 21, 1955)

Article I

ORDER OF BUSINESS

Section 1. At the annual business meeting of the Society, the order of procedure shall be as follows:

Approval of the minutes of last meeting.

Report of the Board of Directors, including those of the Secretary and the Treasurer.

Reports of Standing Committees.

Deferred business.

New business.

Report of tellers of election.

Address of the retiring President.

(This may be presented at another session of the general meeting, at the discretion of the framers of the program of the meeting.)

Section 2. The annual business meeting of the Society shall preferably be on the second day of the general meeting.

Article II

MEETINGS OF THE BOARD OF DIRECTORS

Section 1. The Board of Directors shall hold a regular meeting immediately preceding each general meeting of the Society.

Section 2. Between said meetings the Board of Directors may hold special meetings when called by the President.

Section 3. All meetings of the Board of Directors shall be open to Past Presidents.

Section 4. At the regular meetings of the Board of Directors the order of procedure shall be as follows:

Approval of the minutes of the last regular meeting and of any special meeting the minutes of which have not been approved.

Appointment of tellers of election.

Communications from the President.

Communications from the Treasurer.

Communications from the Secretary.

Discussion of programs of future meetings of the Society.

Reports of Committees.

Deferred business.

New business.

Adjournment.

Section 5. At special meetings of the Board of Directors, the order of procedure shall include the approval of the minutes of the past meeting of the Board and such other of the above items of procedure in their order given as are to be acted upon.

Article III

DUTIES OF OFFICERS

Section 1. The President shall preside at all business meetings of the Society and at those of the Board of Directors. He may represent the Society at any function to which no other particular delegate has been appointed by the Society or the Board of Directors.

Section 2. The Secretary, besides performing the usual duties of that office, shall be the guardian of the records of the Society, collect dues from members, and all bills owing to the Society, and pay such amounts to the Treasurer. He shall report to the Board of Directors at each of its meetings on the condition of the affairs of the Society and make such recommendations as he thinks will facilitate the transaction of the business

affairs of the Society or in any way advance its interests.

Section 3. The Treasurer shall report to the Board of Directors at its meeting immediately preceding the business session of the annual meeting of the Society on the condition of the finances of the Society and make such recommendations as will in his opinion tend to safeguard or improve the same.

Section 4. The Board of Directors shall report to the annual meeting on the general affairs of the Society, including the abstracts of the reports of the Secretary and Treasurer and any other matters which they may consider of interest to the Society.

Section 5. All funds of the Society shall be disbursed on checks signed jointly by the Secretary and Treasurer of the Society, or their agents as authorized by the Board of Directors. For disbursement of regular expenditures they may establish agents funds which are under the control of the Secretary.

Article IV

PUBLICATION COMMITTEE

Section 1. A Publication Committee of three members shall be appointed annually by the Board of Directors. Its Chairman shall be the Editor of all publications of the Society. A second member, called the Technical Editor, shall supervise review of papers submitted for publication. A third member, called the Business Manager, shall handle the financial and business matters of publication. The Publication Committee shall recommend to the Board of Directors the scope and field of activities of the Society's publications.

Section 2. A Committee of Divisional Editors shall be selected by the Chairman of the Publication Committee, subject to the approval of the Board of Directors. This Committee shall consist of at least one representative of each Division of the Society. The Technical Editor shall be Chairman of the Committee of Divisional Editors which shall jointly arrange review of all papers submitted. It shall make recommendations to the Publication Committee concerning acceptance of papers for publication. The Publication Committee shall render a decision on papers as promptly as possible and shall, as occasion permits, assist authors to meet publication standards of the Society.

Section 3. The Publication Committee shall have charge of the publication of the Journal of the Society and shall decide what papers shall be published in the Journal. It shall set final dates for submission of papers and shall establish standards of quality, subject to further provisions of these Bylaws, and to the wishes of the Board of Directors. It shall publish in the Journal such other editorial material and news as it, and the Board of Directors, may deem desirable.

Article V

PROGRAMS

Papers, abstracts, reports, and any material given at the technical sessions of the Society shall be assembled by the joint action of the Officers of the Divi-

sions and the Secretary of the Society. Such papers, abstracts, and reports may be solicited by any of them. The Secretary shall set the date deadline for their inclusion in the technical program, and with the Division Officers shall give or refuse permission for presentation, except that any paper already accepted for publication in the Journal cannot be refused.

Article VI

APPEALS

Appeals from decisions of the Secretary, Publication Committee, or Division Officers may be made in writing by any member to the Board of Directors which has the power to alter or confirm the appealed decision.

Article VII

PUBLICATIONS OF THE SOCIETY

Section 1. Effective January 1, 1948, there is established a monthly publication of the Society to be called "Journal of The Electrochemical Society."

Section 2. The Journal shall contain such technical articles and other additional material as the Publication Committee, which is established in Article IV of these Bylaws, shall determine to publish.

Section 3. Each year the Board of Directors shall, upon the advice of the Finance Committee, set up a budget to cover all expenses of the Journal. The Publication Committee shall operate the Journal within this budget, subject to a review of its operation at each and every meeting of the Board of Directors. Warrants for the payment of bills from the fund thus set up shall be signed by the President and Business Manager and shall be disbursed from the funds of the Society by the officers empowered to disburse the Society funds.

All income to the Journal from advertising and sales of subscriptions shall be received into the General Fund of the Society by the Secretary and Treasurer.

Article VIII

STANDING AND SPECIAL COMMITTEES

Section 1. The following Standing Committees shall be maintained in addition to the Admissions Committee established under Article III, Section 3, of the Constitution: Ways and Means, Finance, Membership, Sustaining Membership, Acheson Medal Award, and Palladium.

Section 2. The President may appoint special committees to conduct investigations or to represent the Society on special occasions.

Section 3. Unless otherwise specified, all committee appointments shall expire with the term of the President who made the appointments.

Section 4. Each Committee shall submit an annual written report to the Board of Directors of its activities.

Article IX

WAYS AND MEANS COMMITTEE

Section 1. The Ways and Means Committee shall act as an advisory group to

the President and Board of Directors on all phases of the Society's business.

Section 2. The Ways and Means Committee shall be composed of seven members. The Chairman of this Committee shall be appointed from among the Board of Directors, and it shall include one Vice-President and at least two Past Presidents of the Society. The members of this Committee shall be appointed by the President immediately upon assuming office.

Section 3. The Ways and Means Committee may carry on its business through subcommittees composed of a Chairman who shall always be a member of the Committee, and such other members of the Society at large as the Chairman of such subcommittees may select.

Section 4. The Ways and Means Committee shall have the power to call on any of the officers of the Society or of its Sections or Divisions to furnish this Committee with such information as it may deem necessary competently to advise the President and Board of Directors as to policies to be followed in the conduct of the Society's affairs.

Section 5. The Ways and Means Committee shall report at appropriate intervals to the President and Board of Directors upon such items of the Society's business as have been referred to this Committee for attention.

Article X

FINANCE

Section 1. The Finance Committee shall consist of five members. The Finance Committee shall assist the Board of Directors in the preparation of a budget and advise the Board on matters of income, expense, and investment of all funds and all other financial operations of the Society.

Section 2. The Finance Committee shall submit a budget to the Board not later than January 15 of the year for which it is to apply. The Committee shall review at each meeting of the Board the operations of the Society and report to the Board its findings.

Section 3. The Committee shall be composed of the following and be appointed by the President: the Treasurer, the Secretary, the Business Manager of the Journal, a Vice-President, and the Chairman of the Ways and Means Committee, unless he holds one of the aforesaid offices, in which event any member of the Society may be appointed in his stead.

Section 4. The Finance Committee shall recommend annually to the Board of Directors a policy of investment of the principal and the allocation of monies which have accumulated in the General Fund of the Society, or in any of the Special Funds under its control.

Article XI

MEMBERSHIP COMMITTEE

Section 1. The Committee on Membership shall maintain a continuing program for the enlargement of the membership of the Society.

Section 2. Each Division and Local Section of the Society shall submit annually to the President the names of two of its members as nominees for the Membership Committee and the President shall, with the approval of the Board of Directors, select one of the persons so proposed as the representative of his Division or Local Section on the Membership Committee.

Section 3. The President shall, in

addition, subject to the approval of the Board of Directors, appoint an additional member of the Committee to serve as Chairman of the Membership Committee.

Article XII

ACHESON MEDAL AWARD

The Acheson Medal Award shall be made by the Board of Directors upon the recommendation of the Acheson Award Committee. The Committee shall function in accordance with the rules accepted and approved by the Board of Directors, March 3, 1949.

Article XIII

ACCOUNTS OF THE SOCIETY

The Board of Directors shall engage a public accountant, not later than December 15th each year, to audit the current accounts and financial statements of the Secretary and Treasurer of the Society. The report of such accountant shall be submitted in such form as to designate the source of all receipts by the Society and the disposition of all funds expended. It shall also include, as far as possible, a statement of the assets and liabilities of the Society so drawn up as to show clearly the net worth of the Society as of December 31st of the year for which the audit is made. The report of the auditor shall be submitted to the Board of Directors through the Treasurer of the Society.

This report shall be printed in the Society's Journal not later than two months after its approval by the Board.

The general results of this audit shall be reported to the members of the Society at the Annual Meeting.

Article XIV

GUESTS AT MEETINGS

Nonmembers may attend technical meetings and social functions of the Society. Requirements for registration of nonmembers may be established by the Local Committee in charge of said functions.

Article XV

SESSION ON ELECTROTHERMICS

At least one session at one general meeting of the Society each year shall be devoted to the subject of Electrotthermics.

Article XVI

DIVISIONS

Section 1. Any member of the Society may register for membership in any Division in which he is interested and may resign therefrom at his discretion.

Section 2. The Officers of the Division shall be a Chairman, one or more Vice-Chairmen, and a Secretary and a Treasurer. The Offices of Secretary and Treasurer may be held by the same person. The above officers, together with two or more members of the Division, shall constitute the Executive Committee of the Division.

The Division shall elect its officers and other members of the Executive Committee during a general meeting of the Society or within thirty days thereafter. The officers and other committee members shall be elected for such terms as the Division Bylaws provide, these terms of office not to exceed two years. An officer may be re-elected, however,

if the Division Bylaws do not prohibit such re-election.

Section 3. A Division shall hold, if possible, one session a year at a general meeting of the Society, such session to be under the auspices of said Division, and publication of papers for such sessions to be subject to the usual regulations and control of the Publication Committee.

Section 4. The Society shall not be responsible for any debts contracted by the Divisions or by the officers thereof. Divisions may receive from the Society such financial assistance as the Board of Directors may determine to be proper, provided such request is accompanied by a financial statement covering the previous fiscal year. It is recommended that each Division submit a financial report within three months of the close of its fiscal year. Such funds shall be used for sending out notices, for solicitation of papers, and for the legitimate work of the Divisions.

Section 5. The Board of Directors may recommend the dissolution of any Division of the Society, such recommendation to be submitted to a vote of the members present at an annual business meeting of the Society.

Section 6. Divisions shall have the privilege of suggesting to the Secretary the names of eligible candidates for officers of the Society. Such suggestions shall be in the hands of the Nominating Committee prior to April 1 each year. The Secretary shall transmit such suggestions to the Chairman of the Nominating Committee when he has been selected.

Section 7. It shall be the duty of the Secretary of the Society to call to the attention of the officers of each Division all of the provisions of Article VIII at least once between January 1st and April 1st each year.

Article XVII

REGULATIONS CONCERNING THE FORMATION AND CONDUCT OF LOCAL SECTIONS

Section 1. Any member of the Society in good standing shall automatically be a member of any Local Section having its headquarters within a radius of fifty miles of said member's residence or principal place of business, provided that he complies with the regulations of the said Section. Members of the Society who live or have their business more than fifty miles from the headquarters of the nearest Local Section may be included in the membership of such Section, provided specific request is made to the Secretary of the Society and approved by the Secretary. Only members of this Society are eligible to membership in its Local Sections.

Section 2. The following provisions shall apply to financial matters of common interest to the Local Section and the Society: (1) The expenses of each Local Section shall be borne by the members enrolled in said Section. The Society shall not be responsible for any debts contracted by a Local Section or by the Officers thereof. Exceptions can be made only in the case of General Meetings for which the Local Section acts as host, as provided in Section 5. (2) Local Sections submitting proof of at least three technical meetings during the fiscal year of the Society will thereupon be granted a sum of fifty dollars each as financial assistance.

Additional financial assistance up to fifty cents per member may be provided

by the Society in each fiscal year, provided the Local Section raises an equal amount from local dues, assessments, or transfer of funds from inactive accounts. Such additional assistance will be made only upon written request of the Local Section, accompanied by a financial statement. This financial statement is due within three months of the close of the fiscal year of the Section. Funds received by Local Sections from the Society as provided herein shall be used solely for the rent of meeting rooms, sending out notices, and paying expenses of persons invited to speak before such Local Sections. (3) Local Sections will receive one dollar from the initial dues of a new member, such sum to be sent to the Local Section by the Secretary of the Society, provided the Local Section was active in securing said new members. To obtain credit for new members, the application must be forwarded to the Secretary of the Society by the Secretary of the Local Section.

Section 3. Papers read before Local Sections, and discussions thereon, if reported, are to be considered as the property of this Society. The Society shall have the first right to publish such papers. Reading of a paper before a Local Section does not carry with it the right of publication in the Journal.

Papers read before Local Sections may be offered for reading at general meetings of the Society, and will be given equal standing with other papers on the program of said meeting, when approved by the Publication Committee.

Section 4. Each Local Section shall transmit promptly after each meeting, to the Secretary of the Society, an abstract of its proceedings, including the titles and names of authors of all papers read before it, for the purpose of preparing a report to the Board of Directors, and for the purpose of enabling the Board of Directors to comply with Section 3.

Section 5.* When a Local Section acts as a host for a General Meeting of the Society, it shall elect one of the following two plans for handling finances of such meetings and shall so advise the Secretary of the Society not less than 90 days prior to the opening of such meeting.

Plan A. The Local Section assumes full responsibility for handling finances of the General Meeting, is responsible for all debts, and may retain any surplus, after paying to the Society a head tax on registrants as determined by the Board of Directors, and provided further that the expenditures of any surplus retained by the Local Section shall be subject to the general approval of the Board of Directors. Local Sections shall submit a complete financial report to the Secretary of the Society as soon as possible after the close of the meeting and in case of a deficit shall notify the Secretary when said deficit has been discharged.

Plan B. The Local Section assists the Board of Directors and the Secretary of the Society in handling the finances of the meeting in its territory, but makes no financial arrangements without the general approval of the Secretary of the Society; the Society shall be responsible for any deficit and shall retain any surplus.

Section 6. Upon the request of a Local Section, the Secretary will endeavor to arrange for an outstanding

speaker to visit such Section, provided the Section will accommodate its meeting date to whatever extent is necessary. The Local Section will be responsible for local expenses of the speaker while he is in their city. Suggestions as to preferred speakers will be welcomed by the Secretary of the Society.

Section 7. Prior to July 1st each year, each Section shall appoint or elect a Councilor to the Council of Local Sections. Such Councilor shall be an active member in good standing in the Society and shall hold office for two years, beginning on July 1st immediately following his or her election, and each Section shall be entitled to two such Councilors. In addition, members of the Society not attached to any Local Section may be placed on the Council by petition of ten members of the Society. Not more than two such Councilors-at-Large may hold office at any one time. Such Councilors-at-Large cannot be from any one locality for more than one two-year term in succession unless a Local Section has been formed in the interim and they thus become regular councilors.

Section 8. The Council of Local Sections shall hold a meeting at each general meeting of the Society. The duties of the Council of Local Sections shall be: (1) to consider problems affecting the welfare and operation of the Local Sections and to work toward their solutions, (2) to act as a clearing house on information, problems, and methods of organization of Local Sections, (3) to act as an advisory council to the Board of Directors of the Society on Local Section affairs, and (4) to make recommendations to the Board of Directors on such other matters relating to the interests of the individual members of the Society as the Councilors may become aware of from time to time.

Section 9. The Council of Local Sections shall elect one of its Local Section Councilors to the Board of Directors at each Spring Meeting of the Council, for a two-year term, and he will be seated immediately at the next meeting of the Board of Directors. During the period a Councilor is a member of the Board of Directors he shall continue to be a member of the Council. The Council shall also elect a Chairman, Vice-Chairman, and Secretary from its Local Section Councilors to conduct the necessary meetings and correspondence of the Council. A set of Bylaws will be adopted for approval of the Board of Directors to guide the formation and operation of the Council.

Section 10. Local Sections shall have the privilege of suggesting to the Secretary the names of eligible candidates for officers of the Society. Such suggestions shall be in the hands of the Nominating Committee prior to April 1 each year. The Secretary shall transmit such suggestions to the Chairman of the Nominating Committee when he has been selected.

Section 11. It shall be the duty of the Secretary of the Society to call to the attention of the officers of each Local Section all of the provisions of Article XVII at least once between January 1st and April 1st each year.

Article XVIII

DUES AND FEES

Section 1. The annual dues for active members shall be fifteen dollars, of which five dollars shall be a non-deductible subscription to the Journal of

The Electrochemical Society. The annual dues for student associate members shall be three dollars, and for associate members nine and a half dollars. Each student associate member and each associate member shall receive the Journal of The Electrochemical Society. The subscription price of the Journal of The Electrochemical Society to non-members shall be set annually before November 1 by the Board of Directors.

Section 2. Any active member of the Society may become a life member upon payment of a life membership fee of \$300 which shall entitle the life member to a life subscription to the Journal and shall relieve said life member of the future payment of annual dues.

Section 3. Emeritus members shall be exempt from the payment of annual dues and shall receive the Journal of The Electrochemical Society without charge.

Section 4. Society Divisions and Local Sections may collect Division or Section dues as authorized by their respective Bylaws.

Article XIX

AMENDMENTS

Amendment to these Bylaws may be proposed by the Board of Directors and shall require a two-thirds vote of the whole Board for their adoption; proxy and mail votes shall be counted when received before the vote is counted. The text of the proposed amendments shall be transmitted to each member of the Board of Directors at least ten days before the meeting at which the vote on the same is to be taken.

New L & N Plant

Another noteworthy addition to the industrial complex of the Delaware Valley advanced recently with the announcement by Leeds & Northrup Company that the contract for construction of its new plant adjoining North Wales, Pa., approximately 22 miles from the heart of Philadelphia, has been awarded to Baton Construction Company, Philadelphia. Occupancy is scheduled for the winter of 1955-1956.

This Leeds & Northrup development is termed the world's most modern control-instrument plant. It will produce such L&N equipment as the various types and models of Speedomax controllers, recorders, and indicators, together with panels and cubicles for certain control applications, and possibly some other L&N products.

Leeds & Northrup officials emphasize that the plant will not replace the long-established headquarters at 4901 Stenton Ave. and other properties in the Germantown section of Philadelphia.

Industrial Survey of Iraq

Final approval has been given by the Iraq Development Board to a contract between the Foreign Operations Ad-

* This section is in the process of being revised.

ministration of the United States Government and Arthur D. Little, Inc., research, engineering, and consulting firm of Cambridge, Mass. This contract has been made at the request of the Government of Iraq and calls for the making of an industrial survey of that country. A plan of action will be determined for the expansion of existing industries and the development of new ones.

Geoffrey D. Roberts is administrator of the project and left Cambridge on December 29 for Iraq. Dr. Lawrence W. Bass, vice-president of Arthur D. Little, Inc., has been working in close contact with the Foreign Operations Administration Mission and the Iraq Government in order to develop the detailed program for the survey.

Although Iraq is one of the oldest civilizations, its potential industrial resources have not been developed. Exploitation of these potentials will enable Iraq to support adequately its population within a very few years. Oil production, with its large number of employees, is the chief industry in the country and has had a marked influence on the development of urban communities. Other growing industries are textiles, cotton and wool production, brickmaking, tobacco, brewing, and date packing.

Iraq is concentrating on the social and industrial development of the country as a means of raising the standard of living for all the people. As part of this long-term planning, an Iraqi Development Board was established by the parliament as an independent agency of the government and given responsibility for administering Iraq's oil revenue and for planning and financing development projects suggested by various government departments. ADL will be assisting and advising this Board in its efforts to further the industrial growth of Iraq.

Specifically, the team from ADL will assess the domestic raw materials now available, potential raw materials, and materials that should be imported; determine industrial opportunities, considering both domestic and foreign markets, determine the physical, economic, and financial factors involved in the manufacturing of industrial products; recommend industries for immediate and future construction; select the industries needing more intense study, and finally determine the capital, human, and technological requirements for this program.

Arthur D. Little, Inc., has had exten-

sive experience in the area development field. At the present time a team of specialists is in Egypt on a three-year industrialization program for that country. ADL has been active in industrial programs both in this country and Canada for many years. A 14-year Puerto Rico assignment called "Operations Bootstrap" has led to tremendous industrial expansion and social and economic progress in that country in the face of very serious problems. In 1952, ADL completed an industrial survey of New England for the Federal Reserve Bank of Boston.

ADL was established in 1886 and is today one of the world's largest research organizations. The late Dr. Little started the organization as a consulting service for the paper industry, when industrial research was in its infancy. Today, it embraces virtually all branches of science and technology.

The country that gave so much culture to the world while North America was still a wild, undiscovered wilderness is now receiving scientific and technological aid from the "new" country across the Atlantic.

Enthone Changes Name of Division

Enthone, Inc., manufacturer of chemical products for metal finishing, has announced a change in the name of its division formerly known as Conn. Metalcraft, Inc. The new name will be Comco, Inc. This corporation has been engaged in the design and manufacture of plating racks, fixtures, filters, plastic tanks, ventilating ducts, and in the sale of general equipment for the electroplating industry. Comco, Inc., is located at 442 Elm St., New Haven, Conn.

NBS Advisory Committees Established

During the past year, 12 technical area advisory committees have been established to provide a direct, continuing link between the National Bureau of Standards and the organized science and technology of the nation. Nine scientific and engineering societies have nominated advisory committees to the Bureau in the fields of physics, chemistry, mathematics, metallurgy, ceramics, and electrical, radio, civil, and mechanical engineering. In addition, the National Conference on Weights and Measures, the American Society for Testing Materials, and the American Standards Association have designated

groups at the Bureau's request to advise in their areas of special interest.

These committees, which will supplement the Bureau's Statutory Visiting Committee, have been set up as a result of recommendations made by the Ad Hoc Evaluation Committee appointed by the Secretary of Commerce in April 1953 to evaluate the Bureau's program in relation to national needs. Under the chairmanship of Dr. Mervin J. Kelly, President of Bell Telephone Laboratories, the Evaluation Committee conducted a comprehensive survey and reported in October 1953 that the Bureau's statutory functions were well conceived and its operations generally sound. At the same time, however, the Committee recognized the desirability of some means whereby the needs of the nation's scientific and engineering societies could be expressed and transmitted to the Bureau for implementation in its program.

In general, the functions of the advisory committees are twofold. First, each committee plays an external role, in which its members represent formally the interests and needs of their society and interpret its point of view in terms of the NBS program. To encourage objectivity in this function, the advisors are nominated by their society and serve as a committee of the society rather than a committee of the Bureau.

The second function, which might be called an internal one, involves assistance to the Bureau on more detailed problems of program formulation and evaluation. Here the committee members work in small groups or panels directly with the heads of the Bureau's various laboratories. Specific advice is given on technical procedures, and suggestions may be made regarding the initiation or possible abandonment of certain lines of endeavor.

The advisory committees have now selected their chairmen and have held one or more meetings at the Bureau. The general areas of interest of the various groups have been largely delineated, and some recommendations have been made. It is felt that the special committees will prove a valuable source of consultation and stimulation which will strengthen the ties of the Bureau with American science and industry.

Technic Opens Chicago Office

For the convenience of electroplaters of precious metals in the Midwest,

Technic Inc. has opened an office at 7001 North Clark St., Chicago 26. Growing use of electroplated precious metals for industrial, scientific, and decorative applications prompted the step, according to Technic officials, to provide prompt on-the-spot service in Chicago and surrounding areas.

Technic Inc. has pioneered in the development of scientifically controlled precious metal plating solutions, equipment, and methods. Products include controlled electroplating equipment, potassium gold cyanide, sodium gold cyanide, rhodium sulfate, palladium plating solution, platinum plating solution, immersion tin, and Protectox silver and copper anti-tarnish.

Yardney Inaugurates Engineering Consultation Service

Yardney Electric Corporation, originators and manufacturers in the U. S. A. of the Yardney Silvercel (Reg. U. S. Pat. Off.), world's lightest, smallest rechargeable storage battery, has organized a new Applications Consultation Department, offering free engineering advice on all battery or portable power source problems.

Staffed by competent engineers, the new service will provide designers with recommendations, at no cost or obligation, as to most efficient solutions for electric power supply requirements, whether or not Yardney silver-zinc batteries would prove to be the most applicable source. The Applications Consultation service will be ready to provide this information for projects in any stage of development.

The installation of this new department is but one more step undertaken by the Yardney organization to offer industry and defense production the best of service, research, and know-how, in addition to its outstanding line of unique lightweight, high-power batteries. Inquiries should be addressed to: Applications Consultation Dept., Yardney Electric Corp., 40-46 Leonard St., New York, 13, N. Y.

Armour Research Foundation Builds Laboratory

A \$1 million laboratory building will be constructed during 1955 by Armour Research Foundation of Illinois Institute of Technology, Chicago, according to Dr. Haldon A. Leedy, director.

The structure—to house the Foundation's electrical engineering research facilities and proposed nuclear reactor—will mark another step in a projected

long-range building program. Construction was scheduled to begin about March 15 with completion by October 1.

Construction of the reactor area of the building will depend on approval of Foundation plans submitted to the Atomic Energy Commission.

Plans for establishing the reactor, the first such facility entirely for industrial research problems, were announced September 29, 1954.

The building will be the fourth constructed for Armour Research Foundation since the Technology Center development program began in 1943. Technology Center is the name applied to the research-study-living area on Chicago's near south side.

Under the new building program, designed to fill the Foundation's needs for expanded physical facilities, the organization anticipates the construction of three new buildings and additions to two existing ones.

Previous Foundation buildings include the Metals Research building constructed in 1943, the Engineering Research building in 1945, and the Mechanical Engineering Research building in 1952.

DIVISION NEWS

Electronics Division

The Committee on Bylaws (A. P. Thompson, H. R. Harner, and J. R. Musgrave) recommends the following revisions. These revisions will be voted on at the annual meeting of the Division during the Cincinnati Convention.

Article I, Section 2

Change to:

- The Electronics Division shall consist of three groups:
- General Electronics
 - Luminescence
 - Semiconductors

(Note: With the admission of the Semiconductor group in 1954, provision is being made for their place in our organization.)

Article II, Section 2

Change (in paragraph 6) to:

All funds . . . shall be dispensed only in accordance with Article V, Section 3b of these Bylaws.

(Note: Correction of typographical error.)

Article III, Section 1

Change to:

The officers of the Division shall be

a Chairman, the Group Chairmen, and a Secretary-Treasurer.

(Note: Change made only for clarification.)

Article IV, Section 2

(Note: Several changes are suggested for clarification. None of the changes affects the previous provisions.)

Change 1st paragraph to: (last two lines)

"Shall make nominations subject to the following rules".

Change paragraph c to:

"The report of the nominating committee shall be made to the officers"

Change paragraph d (last two lines) to:

"before the elections in order that the provisions of Article IV, Section 2-a may be complied with".

Article VI, Section 1

Change Section 1 to:

"The governing body of the Division shall be an Executive Committee consisting of seven (7) or more members. The officers, the representative of the Division on the Membership Committee of the Society, the representatives selected by the Publication Committee of the Society to represent the Division, the editor of the Semiconductor Digest, and the most recent past Division Chairman shall constitute the Executive Committee. No member of the Executive Committee may have more than one vote."

(Note: The change here suggests dropping symposia chairman from the Executive Committee. The reduction in size will make a more workable committee.)

Article VII, Section 1

Change to:

The Division shall hold one business meeting annually, presided over by Division officers . . . following a symposium program.

(Note: This change allows the officers to select an appropriate day for the meeting. Heretofore they were limited to certain days by the old Bylaws.)

Article VII, Section 2

Change to:

The Division shall hold symposia on Electronics, Luminescence, and/or Semiconductors once a year, preferably at the Spring Convention."

(Note: Changes made to reflect wider scope of our activities.)

Article VII, Section 3

Change last sentence to:

"The Chairman . . . may elect to conduct by mail such business . . ."

(Note: Change made for clarification only.)

The Nominating Committee (R. H. Cherry, Chairman, G. E. Crosby, and M. Sadowsky) has selected the following nominees for officers during the 1955-1956 term:

Chairman—Charles W. Jerome (Sylvania Electric Products Inc., Salem, Mass.)

Vice-Chairman (Luminescence)—J. H. Schulman (Naval Research Laboratory, Washington, D. C.)

Vice-Chairman (General Electronics)—C. Dichter (General Electric Co., Syracuse, N. Y.)

**Vice-Chairman (Semiconductors)*—F. J. Biondi (Bell Telephone Labs., Murray Hill, N. J.)

Secretary-Treasurer (3-year term)—Martin F. Quely (Westinghouse Electric Corp., Bloomfield, N. J.)

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

The Bylaws of the Division provide that additional nominations may be made by petition signed by 5 members of the Division. Such petitions must be in the hands of the Nominating Committee before the election and the nominees must have given assurance of their willingness to serve if elected.

The election will be held at the business meeting of the Electronics Division during the Spring Meeting of the Society in Cincinnati.

C. W. JEROME, *Secretary-Treasurer*

Oxide Cathode Symposium

In line with its attempts to provide media for free exchange of experiences in the more practical and materialistic sides of the field of electronically active solid devices, components, and parts, the Electronics Division, under the Chairmanship of Dr. C. P. Hadley of RCA, is sponsoring a symposium on oxide cathodes this year.

Dr. W. B. Nottingham, who is well known to all workers in the field of thermionic emission, will deliver the keynote address for this symposium. His subject will be "Fundamental Phenomena of Thermionic Emission." The symposium will consist of two full sessions devoted to papers covering:

1. Preparation and fabrication of electronically active materials and cathodes.

* Provisional nomination pending formal activation of the Semiconductor Group at the annual meeting.

2. Properties of alkaline earth oxides and also properties of base material, the interface, the coating proper, and the cathode as a whole in conventional coated cathodes.

3. Influences on the properties of cathodes as a function of environment, including considerations of poisoning phenomena, life expectancy, peeling, etc.

4. Thermionic emitters such as L-cathodes, impregnated cathodes, molded cathodes, matrix cathodes, etc.

All who are interested in a more practical side of oxide cathodes are invited to attend this symposium.

A. E. MIDDLETON, *Vice-Chairman*
(*General Electronics*)

Electronics "Enlarged Abstracts" Available

The Electronics Division of the Society will again publish an "Enlarged Abstracts" booklet for the Spring 1955 convention of the Society at Cincinnati. The booklet will have 1000-word abstracts of the papers to be presented before the Electronics Division in its symposia on: Luminescence; Semiconductors; Phosphor Application; Oxide Cathodes. The abstracts will contain pertinent information and experimental data given in the papers and will provide these details before publication, thus aiding workers in the field. The abstracts will be "printed but not published."

The abstract booklets should be available about April 18th; the price will be \$2.00. Orders should be sent to Charles W. Jerome, 60 Boston St., Salem, Mass. Booklets will also be available at the Cincinnati Meeting.

Semiconductor Book Available

Under the sponsorship of the Society, a book, compiled by Battelle Memorial Institute, "Abstracts of the Literature on Semiconducting and Luminescent Materials and Their Applications, 1953 Issue" is being published by John Wiley & Sons, Inc.

Members of the Society who wish to purchase the book, to be sold for \$5.00, at the 33 $\frac{1}{3}$ % member discount should send their orders to Society Headquarters, 216 West 102nd St., New York 25, N. Y. The Society will forward orders to John Wiley & Sons, Inc., who will ship the volume with the invoice. In order to receive the member discount, orders must be sent to Society Headquarters.

Theoretical "Enlarged Abstracts" Available

The Theoretical Electrochemistry Division is publishing for the first time enlarged abstracts of papers to be presented at its symposia at the Cincinnati Meeting of the Society. The booklet will also include abstracts of the Fused Electrolytes Symposia sponsored jointly by the Theoretical Electrochemistry and Industrial Electrolytic Divisions. Copies of the "Enlarged Abstracts" will be available after April 15 at \$2.00 each from Professor Ernest Yeager, Department of Chemistry, Western Reserve University, Cleveland 6, Ohio, and will be on sale at the Registration Desk at the Cincinnati Meeting.

* * *

SECTION NEWS**Chicago Section**

On December 3, 1954, Marvin J. Udy addressed the Chicago Section. Some time was spent discussing National Society business and then Dr. Udy gave some important considerations in Electric Furnace Smelting.

For efficiency in the smelting operation the heat must be generated at the point where it is needed. In commercial practice the way to achieve this is to cause submerged arcing to occur in the slag by passing the current through it. The electrodes for this service are graphite or carbon. The electrode size, shape, and depth of immersion into the slag are important. If the electrodes are too high the arc will strike in the gas phase above the slag, overheating the top of the furnace (not getting the heat into the slag properly). If the electrodes are immersed too deeply into the slag, then no arcing will take place and the total heat generated will be I^2R power. This situation is unfavorable because the control of the furnace cannot be achieved readily by slight changes in electrode height, and also because much of the current is carried by the melt, producing heat in the wrong place. This sometimes results in burning out the bottom of the furnace.

Some other details of over-all design were discussed, including proper current density for the electrodes, the choice of slag depth, and the arrangement of the electrodes so as to give proper current distribution in the slag. Methods of mounting electrodes so as to allow the electrical connections in limited space were included.

J. E. DRALEY, *Secretary*

Three graduate students described their research work at the annual Students' Night meeting of the Chicago Section held on Friday, January 7, at the Chicago Engineers Club.

The first talk, by William S. Ferguson of the University of Illinois, was "Polarography of Fused Salts." Mr. Ferguson discussed polarography in the eutectic system, LiCl-KCl, which melts at 350°C. The low melting point, stability, and high conductivity of this system commend it for study, but the hygroscopic nature of the LiCl is a disadvantage. A Pyrex cell is used with argon as inert atmosphere. Platinum foil serves as the reference electrode, and a rotating platinum microelectrode measures the diffusion current. It was discovered that either Ni(II) or Pt(II) in the solution would set up a reversible cell. The latter salt in the form of K_2PtCl_4 is produced by slow corrosion of the platinum or by anodic action. The decomposition potential of the pure salt mixture is much lower than corresponds to Li and Cl_2 production and indicates the presence of contaminants. Three approaches designed to eliminate traces of water did not give consistent results. Dr. Dole of Northwestern suggested that more stringent purification of the argon is desirable. Various experiments indicated that lithium is completely insoluble in this bath at the temperatures studied. The addition of nickel and platinum salts produced diffusion waves which follow polarographic theory.

Arthur Krawetz of the University of Chicago described his work on "The Use of Raman Spectra in the Study of Equilibrium in Solutions of Strong Electrolytes." The elements of Raman theory were briefly described and the experimental technique was outlined. Raman lines can be predicted from the symmetry of the scattering species. Thus, a certain pattern is always given by tetrahedral structures such as ClO_4^- , IO_4^- , SO_4^{2-} and PO_4^{3-} . These lines can be used to identify the concentration of such species in solution. The mercury arcs of the apparatus are designed to

prevent distillation of the mercury from one arc to the other. The spectrum is observed with a photomultiplier tube cooled with dry ice to minimize noise. The phototube unit is moved automatically to scan the exit radiation. Careful standardization is necessary to make correction for light attenuation, refractive index, and a nonlinear amplification factor. With these corrections, the method is fast and accurate. Data were shown for solutions of H_2SO_4 and HNO_3 from dilute to concentrated. The data are in excellent agreement with published results based on nuclear magnetic resonance.

George A. Lane of Northwestern University discussed "Oxygen Isotope Effects in the Oxidation of Metals." Samples of air taken from an altitude of 32 miles showed apparent enrichment in O^{18} . The samples were taken in steel tanks, and careful study indicated that isotope enrichment was a result of reaction with the vessel walls. By making appropriate corrections based on laboratory data, it was established that the oxygen isotope distribution is the same at 32 miles as at sea level. The isotopic distribution ratio, α , was studied for steel, nickel, cobalt, and sodium. α is nonlinear with pressure. By extending these results to corrosion studies, it may be possible to evaluate oxidation rate law mechanisms.

Each talk was presented with enthusiasm and showed the result of careful preparation. Students' Night is an annual feature of the Local Section calendar and has always been an outstanding meeting.

R. D. MISCH, *Treasurer*

Cleveland Section

Dr. Marvin J. Udy, President of the Society, was the guest of the Cleveland Section at the December 14, 1954, meeting. Following the usual dinner-session, Dr. Udy reported on national affairs of the Society and, at the subsequent evening meeting, discussed the design and construction of electric furnaces.

In his comments concerning the affairs of the Society, Dr. Udy announced the probable balancing of income vs. expenditures during 1954 in spite of the fact that membership dues had decreased by about \$1000. Subscriptions to the JOURNAL have increased to an extent which should largely balance this loss. The need for advertising in the JOURNAL was stressed.

The formation and operation of the

new Local Section council was discussed briefly by Dr. Udy.

Problems relating to financing the cost of the National Convention were discussed, with comments as to possible advertising in the meeting booklet, possible use of the JOURNAL for printing the entire program, etc. In the discussion which followed, the need for definite establishment of conditions under which Local Sections will underwrite the National Convention were emphasized.

Dr. Udy reported that the new Constitution and Bylaws are now being considered and will probably be acted upon in January.

At the evening business meeting, Dr. N. C. Cahoon reported on the arrangements being made for the national convention which will be held in Cleveland in the fall of 1956. He reported that as a result of the death of Joseph Gartland, the Convention Chairman, a replacement had been considered by the Executive Committee and W. Stoll had been recommended, with H. C. Froelich suggested as Vice-Chairman. These appointments by the Executive Committee were confirmed by the membership.

Plans for the joint meeting with The National Association of Corrosion Engineers, scheduled for January 11 at the Manger Hotel, were announced. Dr. H. H. Uhlig of M.I.T. was scheduled to speak.

The appointment of R. S. Johnson as Publicity Chairman was announced.

In his address on Electric Furnaces, Dr. Udy discussed smelting or slagging furnaces from the viewpoint of the chemist or metallurgist, primarily, rather than from the viewpoint of the production or design engineer. Based upon his many years of experience, Dr. Udy pointed out some of the requirements for successful design and operation as they are related to the electrode consumption, preservation of the furnace itself, and our requirements. Dr. Udy pointed out that, in general, an arc formed by an electrode located appreciably above the molten slag is inefficient and will not produce a satisfactory smelting condition. On the other hand, the submersion of the electrode more than three inches below the surface of the molten slag leads to erratic consumption of the electrode and difficulty of control. With the arc near the surface, control of individual power circuits in multielectrode furnaces is possible and by careful adjustment the metal below the slag can be kept molten without overheating of the furnace. Dr. Udy

pointed out that continuous tapping of the molten materials is desirable for smooth operation.

The talk was well illustrated with a series of slides which showed relationship between peripheral ohms and electrode requirements, as well as other operating details. Following a discussion of the talk, the meeting was adjourned.

K. S. WILLSON, *Secretary*

India Section

The third technical meeting of the India Section was held on December 24, 1954, at Mettur Dam in the premises of Mettur Chemical & Industrial Corporation Ltd., Mettur Dam R.S. Mr. R. Natarajan, Secretary of the corporation, was the Chairman of the evening. Mr. S. Ramaswamy, Production Superintendent, Mettur Chemical, gave a talk on "German Electrochemical Industry."

The lecturer traced the development of the electrochemical industry in Germany and added that the electrochemical industry combine was broken up into small units. He discussed two lines of production: (a) caustic soda and chlorine, and (b) calcium carbide. Various cells in the production of electrolytic chlorine industry of Germany were described, and the production figures for chlorine from 1940-1954 were given. The main chlorine plants are situated in Gendorf, Burghausen, Hoechst, Rheinfelden, Huels, Knapsack, Luelsdorf, and Leverkusen in West Germany. The majority of the plants make use of mercury cells while a small proportion of the industries employ Billiter type cells. The lecturer described the working of some of the plants in detail, and listed the various by-products of caustic soda and chlorine. An interesting development in Germany is the production of various products from the sodium amalgam of the chlorine cell, apart from making caustic soda. Nearly water-white sodium sulfide is one of the products from sodium amalgam.

Mr. Ramaswamy narrated the development of the calcium carbide industry in Germany. All the plants follow the same process, i.e., the electric furnace feed, lime, anthracite, and coke. Consumption of electricity of the furnace is about 3100 kwhr/ton of calcium carbide CaC_2 of 290 l/kg quality. He discussed the capacity of various plants in Germany and gave operating details. The major portion of carbide in Germany is converted in the plant itself to calcium cyanide and to acetylene which forms the starting point of various chemical products.

Electrochemical industry in Germany has been revived on a large scale after the war and many of the plants have been modernized.

With a vote of thanks to the speaker and to the management of Mettur Chemical & Industrial Corporation Ltd., the meeting came to an end.

S. KRISHNAMURTHY, *Secretary-Treasurer*

Philadelphia Section

The Philadelphia Section's January meeting was addressed by Mr. John W. Tiley and Dr. Edmond H. Borneman of the Philco Corporation. They described work carried out by themselves and Dr. Richard Williams on surface barrier transistors. Mr. Tiley introduced the discussion by outlining the history of transistors, emphasizing the advantages and shortcomings of some of the earlier types. Dr. Borneman reviewed briefly the fundamental principles of the behavior of transistors, following this with a detailed explanation of the electrochemistry involved in the production of Philco's surface barrier transistor. Mr. Tiley then demonstrated, with the aid of some excellent motion pictures, the actual fabrication of these devices. The process depends upon the electrochemical etching of two tiny depressions on opposite sides of a thin wafer of a germanium crystal at the point of impingement of two very fine streams of an electrolyte solution. By reversing the direction of the current, a small button of a metal such as indium is then deposited in these depressions. The attachment of suitable leads and sealing of the unit completes the process. The audience responded enthusiastically with questions at the end of this interesting and informative dissertation.

Prior to the technical session about forty members and guests had the pleasure of meeting the speakers at a social hour and dinner.

GEORGE W. BODAMER, *Secretary*

NEW MEMBERS

In January 1955 the following were approved for membership in The Electrochemical Society by the Membership Qualifications Committee:

Active Members

ROBERT CLARK, Atlas Steels Ltd., Welland, Ont., Canada (Electrothermics and Metallurgy)
WILLIAM R. DEHOLLANDER, General Electric Co., Mail add: 2207 Putnam,

Richland, Wash. (Industrial Electrolytic, Theoretical Electrochemistry)
RALPH J. GREEN, Westinghouse Electric Corp., Mail add: 531 Summer Ave., Newark 4, N. J. (Electrodeposition, Electronics, Electrothermics and Metallurgy, Industrial Electrolytic, Theoretical Electrochemistry)
JAMES F. HIGGINS, Phelps Dodge Refining Corp., 43-09 55th Dr., Laurel Hill, Maspeth 78, L. I., N. Y. (Electrodeposition)
GEORGE A. HILLMAN, Melpar, Inc., Mail add: 1630 Wisconsin Ave. N.W., Washington 7, D. C. (Electrodeposition)
RICHARD A. HUMPHREY, Mycalex Corp. of America, Mail add: 125 Clifton Blvd., Clifton, N. J. (Electric Insulation)
MICHAEL J. JONCICH, Dept. of Chemistry, University of Tennessee, Knoxville 16, Tenn. (Theoretical Electrochemistry)
DOUGLAS S. KEIR, Kaiser Aluminum & Chemical Corp., Mail add: W. 1014 24th Ave., Spokane, Wash. (Corrosion)
HAROLD KWART, Dept. of Chemistry, University of Delaware, Newark, Del. (Electro-Organic)
ROY G. POST, General Electric Co., Mail add: 631 Cottonwood, Richland, Wash. (Corrosion, Electrodeposition, Theoretical Electrochemistry)
PAUL E. RITT, Melpar, Inc., Mail add: 1326 S. George Mason Dr., Arlington 4, Va. (Electrodeposition, Electronics)
ROBERT C. SHAIR, Bell Telephone Laboratories, Inc., 463 West St., New York 14, N. Y. (Battery)
LEBO R. SHIOZAWA, Brush Laboratories Co., Mail add: 2026 E. 107 St., Cleveland 6, Ohio (Corrosion, Electronics)
JULIAN S. SMITH, Johns Hopkins University, Mail add: 1311 Park Ave., Baltimore 17, Md. (Electronics)
RODNEY B. TEEL, INCO Kure Beach-Harbor Island Testing Station, Mail add: 43 Lee Dr., Lake Forest, Wilmington, N. C. (Corrosion)
WILLIAM J. THOMSON, Simonds Canada Abrasive Co. Ltd., Mail add: 926 Coulomb St., Arvida, Que., Canada (Electrothermics and Metallurgy)
FRANK P. WILLIAMS, Kaiser Aluminum & Chemical Corp., Permanente, Calif. (Battery, Electrodeposition, Electrothermics and Metallurgy)
WILBUR J. WILSON, Batelle Memorial Institute, Mail add: 225 Orchard Lane, Columbus 14, Ohio (Electrothermics and Metallurgy)
EUGENE A. WINIARSKI, Chemical Laboratory, Philco Corp., "C" & Tioga

Sts., Philadelphia, Pa. (Electrodeposition)

HYMAN W. ZUSSMAN, Geigy Industrial Chemicals, 89 Barclay St., New York 8, N. Y. (Corrosion)

Associate Members

WILLIAM J. HAESSLY, National Carbon Co., P.O. Box 6087, Cleveland 1, Ohio (Battery)

DEAN L. TODA, National Carbon Co., Mail add: 4086 Ridge Rd., Cleveland 9, Ohio (Battery)

Student Associate Member

ARMAND P. BOND, Massachusetts Institute of Technology, 521-A Graduate House, Cambridge 39, Mass. (Corrosion)

PERSONALS

J. C. WARNER, Past President of The Electrochemical Society, has been chosen President-Elect of the American Chemical Society. Dr. Warner is president of Carnegie Institute of Technology, Pittsburgh, Pa.

DWIGHT E. COUCH, physical chemist, has rejoined the staff of the National Bureau of Standards, Washington, D. C., where he will conduct research on the electrodeposition of molybdenum. Prior to rejoining the Bureau, Mr. Couch was with the Naval Ordnance Test Station at China Lake, Calif., where he was engaged in research and development in the fields of electrodeposition and corrosion. He was a member of the Bureau staff working on electrodeposition from 1948 to 1952.

EDWARD ORBAN of Miamisburg, Ohio, has been transferred to the development department of Monsanto Chemical Company's Inorganic Chemicals Division in St. Louis. Dr. Orban was previously chief of the technical information section at Mound Laboratory operated by Monsanto at Miamisburg for the Atomic Energy Commission.

TAKASHI MUKAIBO, previously an assistant professor at Tokyo University, has joined the staff of the Japanese Embassy in Washington, D. C., as Scientific Attaché.

JOHN H. ZAUNER, formerly chief engineer at Mills Industries, Inc., Chicago, is now general manager of the

Henry L. Crowley Co., West Orange, N. J. The company manufactures magnetic ceramics (ferrites), steatites, and powdered iron parts, principally electronic components.

KENNETH B. MEYER has accepted a position as chemical engineer with Sprague Electric Co., North Adams, Mass. Mr. Meyer is studying aluminum for use in electronic condensers and doing development work on this type of electrolytic condenser. He was previously a technologist with National Lead Co. in Cincinnati.

BOOK REVIEWS

DIELECTRICS AND WAVES. Edited by Arthur R. von Hippel. Published by John Wiley & Sons, Inc., New York, and Chapman & Hall, Ltd., London, 1954. 284 pages, \$16.00.

"Dielectrics and Waves" presents the basic physical and electromagnetic theory which underlies the subject of dielectrics. Dielectrics are defined as materials other than the metals.

Part I entitled the Macroscopic Approach gives a detailed development of the essential relationships for permittivity and permeability for the entire spectrum of frequencies from direct current up. The interaction between electromagnetic waves and dielectric materials from a molecular and quantum mechanical point of view is considered in the somewhat longer Part II.

There are sections on microwave spectroscopy, ferroelectricity, paramagnetism, and ferromagnetism, in addition to sections on polarization, dipole moments, and other relevant topics.

With its companion volume, "Dielectric Materials and Applications," it provides the tools for an understanding of dielectric behavior.

S. O. MORGAN

DIELECTRIC MATERIALS AND APPLICATIONS. Edited by Arthur R. von Hippel. Published jointly by the Technology Press of M.I.T. and John Wiley & Sons, Inc., New York, and Chapman & Hall, Ltd., London, 1954. 437 pages, \$17.50.

The first section of this book contains a brief review of dielectric theory written by Professor von Hippel. Following this is a section on Measuring Techniques by five authorities, and then a section on Materials and Applications by thirteen well known in their respective

fields. A brief section describes the special requirements of the Armed Forces by representatives of the Air Force, Army, and Navy. The final third of the book consists of tables and curves of dielectric data compiled from measurements of the Laboratories for Electrical Insulation. There is also a useful materials index to these tables.

The theory given in this volume is an abridgment of the material in the companion volume, "Dielectrics and Waves." It is extensive enough to satisfy the needs of most users of dielectrics. The sections on Dielectric Measuring Techniques and on Dielectric Materials and Their Applications are essentially the same as the material presented in 1952 at the Summer Session Course of the Laboratory for Insulation Research at M.I.T. The 125 pages of tables and curves of dielectric properties of a wide variety of materials are measurements made at the Laboratory for Insulation Research and heretofore not generally available.

This book will be indispensable to anyone seriously concerned with the understanding and development of dielectric materials.

S. O. MORGAN

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LITERATURE FROM INDUSTRY

VACUUM TUBE ELECTROMETERS. New 12-page catalogue describing vacuum tube electrometers and accessories has been released. Designed in part as a manual for engineers and scientists, the catalogue includes introductory data on electrometer characteristics, circuit discussions, and equipment photographs. Seventeen connection diagrams show how the instruments are used as ultra-high input impedance d-c millivoltmeters, voltmeters, and kilovoltmeters; sensitive microammeters and micro-microammeters; accurate megohmmeters, megmegohmmeters, d-c preamplifiers, and static detectors. Keithley Instruments. P-273

PRECISION CLEANING AND FINISHING. Precision cleaning and finishing is the subject of a comprehensive brochure recently published. Dealing with the wet abrasive blasting process, the 18-page booklet presents 40 frequently met applications in which this process can be profitably used. A section is devoted to describing the process, itself, in which water-suspended abrasives are thrown at high velocity upon the work. Necessary equipment is also mentioned. Some applications listed are: blending directional lines of finish; reducing glare on metals; preparing metallic parts for anodizing, plating, painting, inspection, repairing, or rebuilding; deburring; degreasing. American Wheelabrator & Equipment Corp. P-274

PROTECTIVE ATMOSPHERES IN HEAT TREATING. Bulletin describes the use of protective atmospheres to prevent deterioration of metals during various heat-treating processes. Designated as GEA-5907, the 12-page publication explains G.E.'s four basic types of gas-producing equipment which meet most protective atmosphere needs. Case histories illustrate the savings to be made in different types of jobs. Two tables are included: one is a selection guide to help choose the correct protective atmosphere for each job, and the other explains the approximate compositions and costs of producing typical protective atmosphere gases. General Electric Co. P-275

ELECTRONIC GAUGER SYSTEM. Application data sheet describes an electronic gauger system widely used in pipeline operations. This 4-page bulletin describes and illustrates principles of operation, equipment, circuitry, and the use of HELIPOT (Reg. U. S. Pat. Off.) precision potentiometers in this telemetering system. Available on request. Helipot Corp. P-276

ENTHONE ENSTRIPS. Illustrated folder is available which describes Enthone ENSTRIPS. These are materials for selective stripping of one metal from another. For example, nickel from steel or copper, tin or tin-lead from copper or steel, and copper from steel. A handy chart is given for easy selection of the proper stripper for any particular job. Enthone, Inc. P-277

TITANIUM TUBING. Tubing of titanium, the promising and still comparatively new metal whose potential usefulness has just begun to be realized,

is the subject of a recently published bulletin. The 8-page publication presents the most up-to-date information on the fabrication of unalloyed titanium tubing. Subjects covered include heat treating, pickling, welding, brazing, and machining. A separate section on corrosion resistance gives details on titanium's behavior with many of the common reagents. Superior Tube Co. P-278

DOW PRODUCTS. A newly revised catalogue entitled "Products of The Dow Chemical Company" provides an alphabetical listing of Dow chemicals. Prepared in brief form, the booklet is available upon request. Dow Chemical Co. P-279

"BULK CHEMICALS." New Fisher chemical supplement serves notice that the same high-purity lot-analyzed reagents known to researchers are now available to manufacturers and pilot-plant engineers as well, in 100 to 600 lb drums available for immediate delivery. Fisher Scientific Co. P-280

METAL PROTECTION & PAINT BONDING. Data sheet gives a concise description of chemicals for metal protection and paint bonding for aluminum, zinc, and steel. Also included is a metal and process index. American Chemical Paint Co. P-281

"ENGINEERED PERFORMANCE." Brochure tells about the growing significance of graphite in electrometallurgy and electrochemistry, and outlines some reasons why the Electrode Division, Great Lakes Carbon Corporation, has made such steady progress as a graphite supplier. Free copy available upon request. Great Lakes Carbon Corp. P-282

NEW PRODUCTS

ONE-SOLUTION "DISTINGUISHER." Here is a new way to sort Pyrex-brand glass from soft glass and quartz glass in laboratories, institutes, chemical stockrooms, universities, and hospitals. A



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University of Kentucky professor discovered accidentally that mixing 59 ml of carbon tetrachloride and 41 ml of benzene in a jar gives a "distinguisher" with a refractive index of 1.472, about that of Pyrex-brand glass. Thus, when an assortment of pipettes or other glassware was placed in the jar, the Pyrex-brand glassware became invisible, while the soft glass was clearly outlined. Now, Fisher Development Labs. chemist J. D. Bode has come along with a *one-liquid* "distinguisher." He noted recently that the walls of a thick Pyrex-brand glass vial disappeared when the vial was filled with reagent-grade *trichloroethylene*. Under the same conditions, soft glass and quartz remained completely visible. Fisher Scientific Co. N-145

FILTER UNITS. Design, manufacture, and sale of a new series of cartridge type filter units designed especially for the electroplating and electroforming industries have been announced. The units are available in a variety of models ranging from 100 gallons to 5000 gallons or more per hr. Available in iron, stainless steel, rubber, and plastic for use with all types of corrosive solutions. Easy to assemble and disassemble. Cartridges woven with a variety of fabrics to withstand solutions can be used, including cotton, dynel, orlon, glass, acetate, and nylon. COMCO, Inc., Division of Enthone, Inc. N-146

KER-CHRO-MITE GZ. Newly developed olive green conversion coating for zinc is chromate type and is supplied in stable concentrated solution which is cut to desired strength for use on zinc. The process imparts a uniform olive green coating on zinc which passes 100 hr of salt spray test to formation of white oxides. The bath once made will not break down easily. It is used at room temperature or colder. The working bath needs only periodic replenishment with the concentrate. The film formed has excellent properties as a base for paint or as an attractive olive green finish. Adaptable to all Federal Ord-

nance finishes requiring this type of high corrosion protection as well as uniformity of color. Kosmos Electro-Finishing Research, Inc. N-147

GERMANIUM OPTICAL FILTER. First optical filter made from germanium is now being offered. The germanium infrared transmission filter will introduce a series of optical products made from transistor materials soon to appear on the market. It is fabricated from a highly purified germanium single crystal. It is $1\frac{1}{2}$ in. in diameter and $\frac{1}{8}$ in. thick, and is ground, polished, and coated on both sides. Due to the high refractive index of germanium, the plates are antireflection-coated for maximum transmission at 2.5μ . This infrared filter absorbs wave lengths shorter than 1.8μ and transmits both the near and far infrared regions of the spectrum. It is particularly well suited for use with lead sulfide infrared photodetectors. Baird Associates, Inc. N-148

SELENIUM RECTIFIERS. Now in production is a series of hermetically sealed, high voltage selenium rectifiers for use in airborne equipment where adverse atmospheric conditions, severe vibration, and rigid electrical specifications must be met. A complete line covering an input voltage range from 33 v to 660 v is available for many airborne applications, including fire control and radar systems. Engineering data to meet your specific applications and/or bulletin available upon request. International Rectifier Corp. N-149

VACUUM GAUGE TUBE. Newly designed vacuum gauge tube, designed to retain permanent calibration while withstanding intense vibration, shock, and temperature change has been announced. For use with the Hastings Vacuum Gauge and Hastings Vacuum Indicator-Controller in the 1-1000 μ range. Sensing elements of the tube are short, butt-welded noble metal thermocouples. The couples are arranged in a thermopile so as to compensate for temperature changes and even rate of change in temperature. Welded construction makes the tube particularly resistant to damage by vibration. Hastings Instrument Co., Inc. N-150

HIGH-FREQUENCY TITRIMETER. New Fisher High-Frequency Titrimeter (Reg. U. S. Pat. Off.) whose metal electrodes never come in contact with the solution has been introduced. There is nothing in the titration vessel but the solution

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Bell Telephone Laboratories, Inc.	150
Enthone, Incorporated	Cover 4
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and a polyethylene (or glass) coated stirrer-magnet. With this new instrument there is no problem of maintaining delicate platinized electrodes . . . no electrolysis of the sample . . . no polarization or "smothering" of the electrodes by precipitates. High-frequency titrations can be carried on in organic solvents and mixtures of solvents. They can be used to assay traces of acid or other impurities in such liquids, and in lubricating oils and other petroleum products. Fisher Scientific Co. N-151

NEW REAGENTS EXPEDITE ELECTROPHORESIS. Paper electrophoresis is bringing a whole new realm of techniques to chemists, pathologists, serologists, and biologists. To make this method more convenient than ever before, Fisher Scientific has produced—in handy, individual, factory-sealed laminated packets—three high-purity aids for the analysis of blood proteins on the widely used Spinco Paper Electrophoresis Apparatus. This is the first time that such materials have been made available in contaminant-free, disposable, "rinse-out" envelopes. Fisher Scientific Co. N-152

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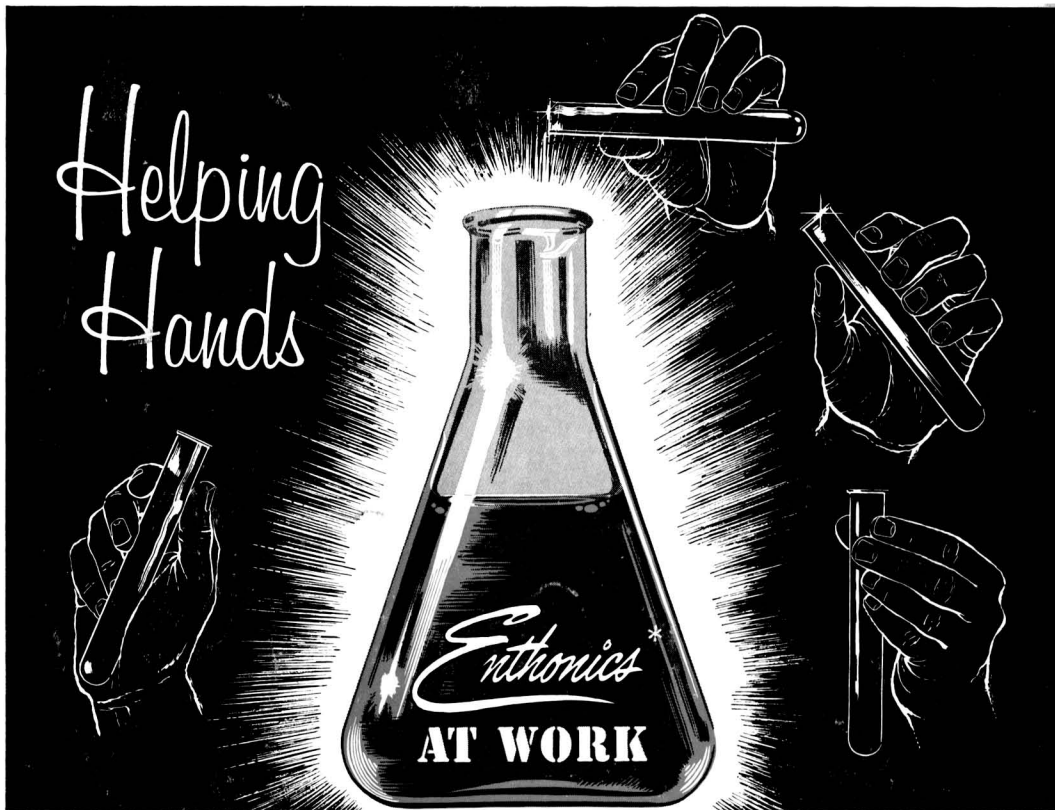
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