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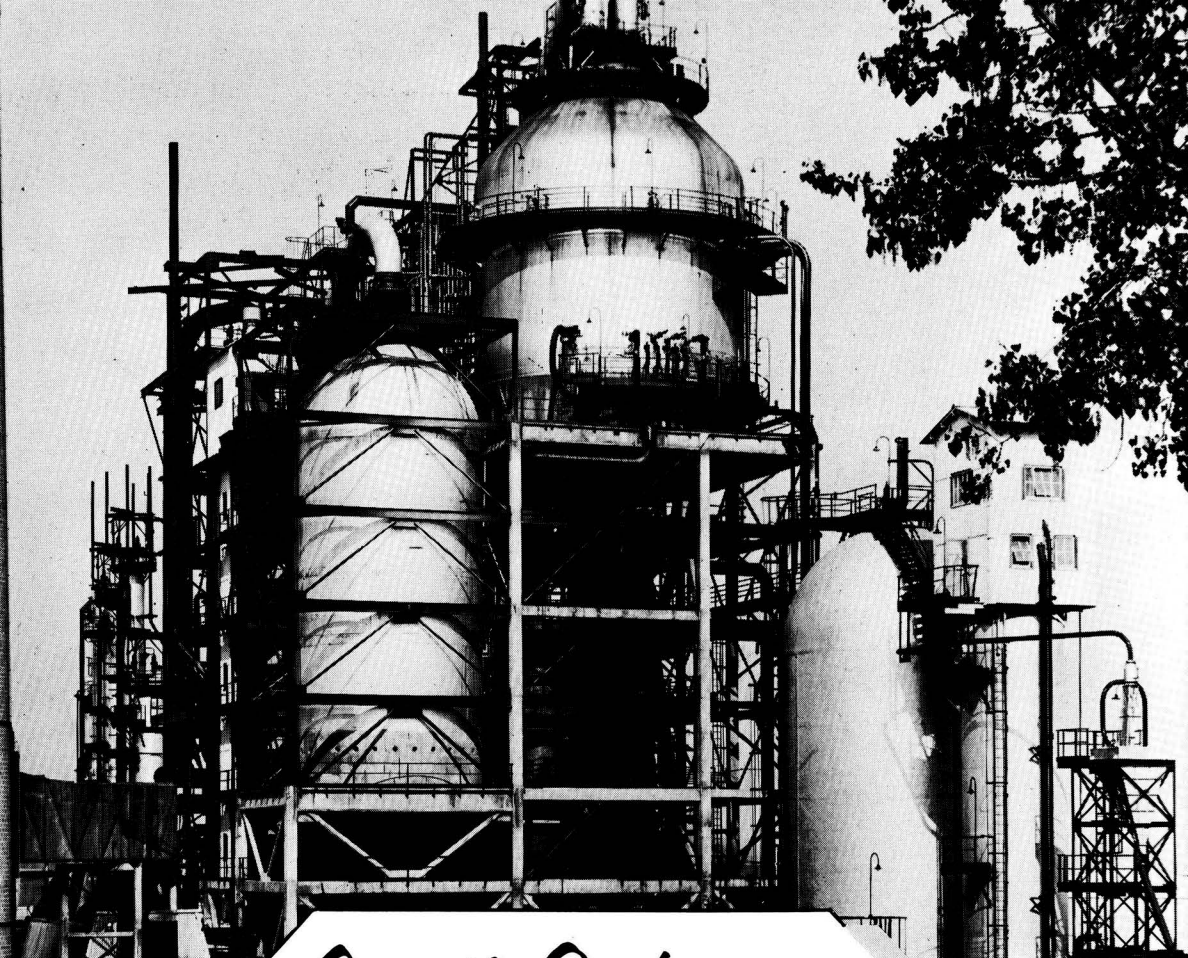


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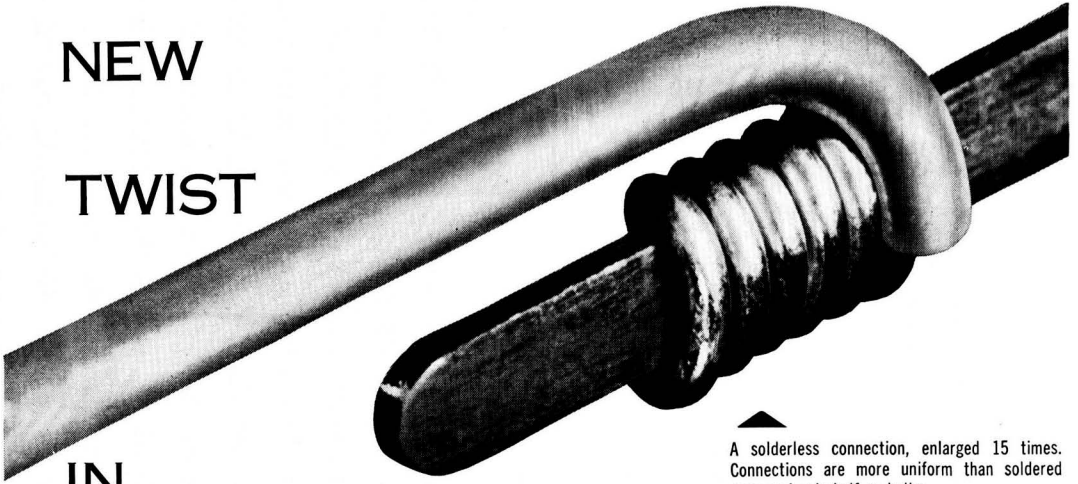
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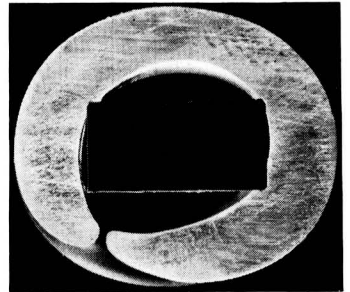
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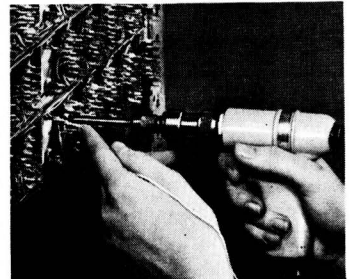
The new connections can be made in half the time—a big money-saver in the billion connections that Western Electric makes each year for the Bell System. It's another example of the way Bell Telephone Laboratories works continually to keep costs low.

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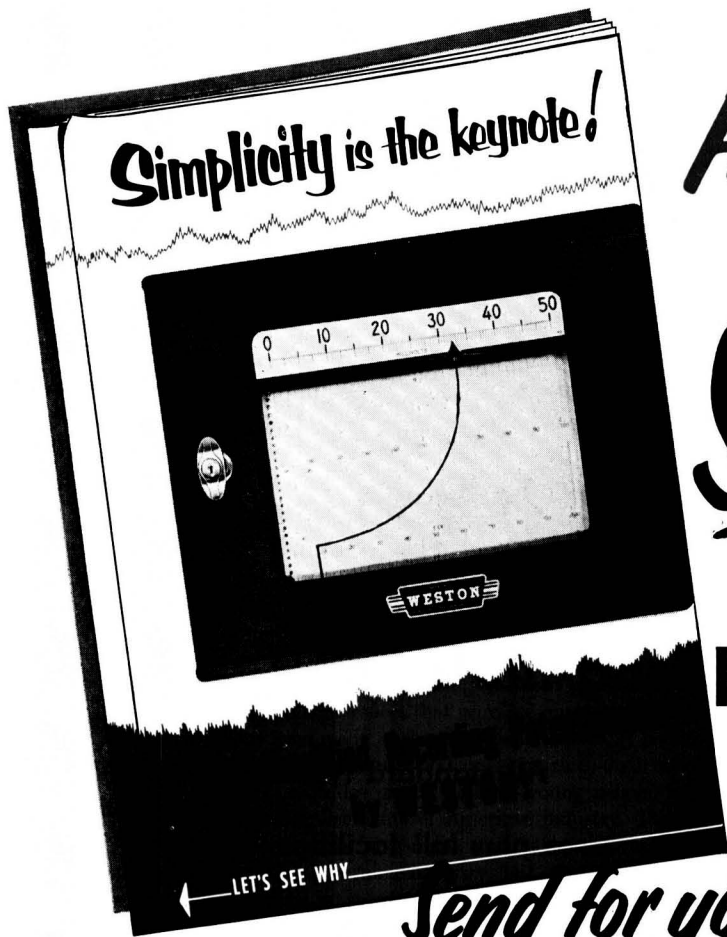
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Promotion of Industrial-Educational Understanding

THE founding of the Industrial Council by Rensselaer Polytechnic Institute as a medium of communication and understanding between industry and education should prove to be a significant contribution to the American free enterprise system. The activity of the Council consists in the presentation of a two- or three-day program arranged by the Institute, held on its campus and devoted to the portrayal of American industry, its characteristics, its problems, and its contributions to modern life. At each session, an important industrial group acts as host and invites as its guests the teachers of social studies from secondary schools and colleges in all parts of the country. The first session was sponsored by the oil industry; the second, held last May, by the chemical industry. This month the electrical industry will be host at the third convocation.

The program of the chemical meeting consisted of addresses by several leaders of the industry, followed by 18 panel conferences that provided opportunities for detailed discussions stimulated by the questions from many of the 800 teacher-guests. It became apparent in the course of the discussions that these teachers, who have so much to do in conditioning the minds and shaping the thinking and attitudes of the nation's young people, had very little knowledge of the character and accomplishments of American industry. The viewpoint of many of them reflected their exposure to labor-union and left-wing propaganda; others reported that they sought information concerning industry, but were forbidden by timid or "psychoceramic" school authorities to make use of the limited amount of material received from industrial sources. However, in some more enlightened areas of the country, teachers may choose their material from even such sources as the National Association of Manufacturers. It was gratifying to note that the teacher-guests attending the recent meeting readily accepted the excellent "Facts Book of the Chemical Industry," just issued by the Manufacturing Chemists Association.² This is a 108-page booklet of up-to-date and fascinating information concerning the chemical industry.

It is clear that industrialists as well as teachers profit from their attendance at meetings of the Industrial Council. Industries supporting this project are to be complimented for their contribution to public education and ultimately the general welfare.

Trygve Lie, who addressed the first session of the Council, stressed the broad significance of its work in the following words:

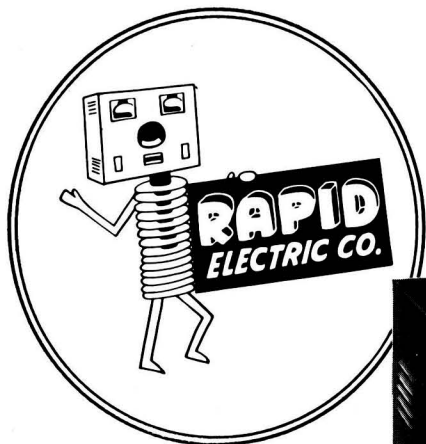
"Wider understanding and knowledge of the great industries that play so central a role in the life of our times is certainly important both for individual nations and for the world. To bring together, as you are doing, the leaders of one great industry after another, starting with the oil industry—with writers, teachers, and students specializing in history, economics, and sociology—seems to me a practical and sensible contribution to this end. As Secretary General of the United Nations, I have a special interest in all efforts to promote wider understanding of the world we live in, of the many forces at work in the world, and how these forces can affect the progress toward the main goals of the United Nations—a more secure peace, wider freedom, more equal opportunity, and higher standards of living for people in all parts of the world."

—RMB

¹ Current American vernacular for "crack-pot."

² Procurable from Manufacturing Chemists Association, Woodward Building, 15th and H Streets, Washington 5, D.C. Price \$1.00.

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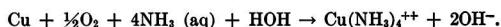
Kinetics of the Dissolution of Copper in Aqueous Ammonia¹

J. HALPERN

University of British Columbia, Vancouver, Canada

ABSTRACT

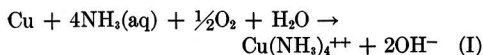
Copper reacts readily with aqueous ammonia in the presence of oxygen, as follows:



The kinetics of this reaction were investigated over a wide range of NH_3 and NH_4^+ concentrations, oxygen pressures, temperatures, and stirring velocities. The rate of dissolution was proportional to the surface area of the copper, and, at low oxygen pressures, was determined by the transport of dissolved oxygen to the surface. When the pressure of oxygen, above the solution, was increased, the chemical reaction at the surface became rate-controlling. Two dissolution reactions were found to proceed simultaneously and with independent rates, which were first order with respect to the concentrations of NH_3 and NH_4^+ , respectively. Both were independent of the concentration of oxygen. Mechanisms have been proposed for these reactions, consistent with the observed reaction products and kinetic results.

INTRODUCTION

In the presence of oxygen, copper dissolves readily in aqueous ammonia in accordance with the following reaction:



Earlier investigations of the kinetics of this reaction (1-3) have provided conflicting information about the reaction order and about the roles of ammonia, oxygen, ammonium ion, and cuprammonium ions in the reaction. For example, Yamasaki (1) reported autocatalysis by cuprammonium ions, and found the rate of dissolution to be independent of the concentrations of ammonia or of salts in the solution. On the other hand, Lane and McDonald (3), in a more recent study, failed to observe any evidence of autocatalysis, and found instead a strong dependence of the rate on ammonia concentration. The effect of oxygen pressure on the rate has also been variously described, and all the earlier investigators found that the rate increased markedly with stirring velocity, indicating that it was controlled, in part at least, by the transport of oxygen through the solution to the copper surface. Another feature observed (1) was the formation of a coating of insoluble products on the copper surface at low ammonia concentrations. Diffusion of the reactants or

products through such a film might also contribute to determining the rate of the reaction.

Complicating features, such as these, might have been responsible for the discrepancies in the observations of earlier workers, for it is well known that when a physical process, such as diffusion of a reactant, controls the rate of a chemical reaction, the effect on the rate, of other variables and of the concentrations of other reactants, is masked, and kinetic results provide little information about the mechanism of the reaction.

In view of this, it appeared desirable to re-investigate the kinetics of this reaction under conditions where the chemical process itself was rate-controlling, where no insoluble products were formed, and where the transport of oxygen to the copper surface was sufficiently fast that it did not influence the rate. The last condition is particularly important and was achieved, in the present study, by maintaining a high partial pressure of oxygen above the solution. This permitted the kinetics of the reaction to be investigated over a wide range of ammonia and oxygen concentrations, together with the examination of other variables such as pH, temperature, stirring velocity, and the concentrations of NH_4^+ and other salts.

EXPERIMENTAL

Materials

Reagent grade ammonia and other chemicals used in making up the solutions were supplied by Nichols Chemical Company. Oxygen was supplied in cylinders by Canadian Liquid Air Company and used without further purification. Pure copper, in the form of rods of 1.59 cm diameter, was supplied

¹ Manuscript received February 9, 1953. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952. Contribution from the Department of Mining and Metallurgy, University of British Columbia. This work was supported by funds provided by the Atomic Energy Control Board and administered by the National Research Council of Canada.

by Anaconda Copper and Brass Company. Spectrographic analysis² indicated a purity of 99.98+ per cent. The rods were cut into disks about 1 cm thick, which were mounted in Bakelite to insulate them electrically and to leave exposed only a desired surface cross section of copper, normally 2.0 cm² in area. This surface was polished prior to measurement of the dissolution rate. Alternative methods of preparing the surface, such as etching with NH₃ or HNO₃, were found to give identical dissolution rates.

Apparatus

The apparatus used in this study is described in Fig. 1, and was constructed entirely of stainless steel, which was inert to the solutions used. The vessel measured 7 in. ID by 11 in. in height, and was

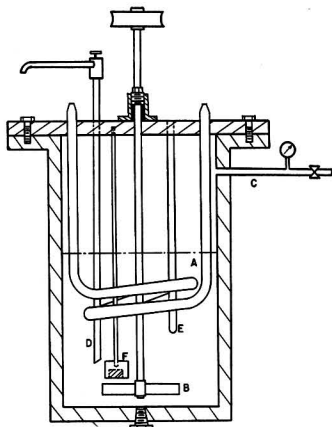


FIG. 1. Diagram of stainless steel pressure vessel and internal parts. A—Heating coil; B—stirrer; C—gas inlet tube; D—sampling tube; E—thermometer well; F—copper specimen in Bakelite mount.

designed for pressures up to 10 atm. The Bakelite mount containing the insulated copper specimen was held by a stainless steel rod, so that the copper surface was exposed to the solution about 5 mm above the blade of the stirrer. The stirrer was 10.9 cm in diameter and its speed of rotation could be varied from 400 to 900 rpm. A volume of 3 liters of solution was normally used, and its temperature maintained to within $\pm 0.5^\circ\text{C}$ of a given value, by passing steam or cooling water through the coil, A. The pressure of oxygen, above the solution, was controlled with a standard gas regulator, allowing for the partial pressures of water and ammonia.

Procedure

The course of the reaction was followed by withdrawing samples of the solution through the tube,

² Kindly carried out by Department of Mines, Victoria, British Columbia.

D, at measured time intervals, and determining the concentration of dissolved copper by the carbamate method (4) using a Beckman Model DU spectrophotometer. From these values and the known volume of solution and surface area of copper, the amount of copper dissolved per unit area of surface could be calculated. Ammonia concentrations were measured by potentiometric titration with standard HCl. Each experiment lasted between 3 and 6 hours during which approximately 10^{-3} moles/l of Cu was dissolved. This amount was insufficient to cause an

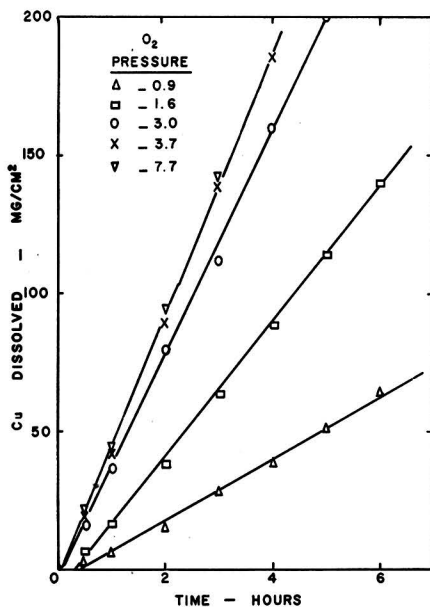


FIG. 2. Rate curves for the dissolution of copper in aqueous ammonia at various oxygen pressures. Total NH₃, 0.74 mole/l; temperature, 26°C; stirrer velocity, 660 rpm.

appreciable change in the concentration of ammonia through the formation of $\text{Cu}(\text{NH}_3)_4^{++}$.

Rate Curves and Products of the Reaction

Rate curves for the dissolution of copper in ammonia were always of the form shown in Fig. 2. The amount of copper dissolved was proportional to the reaction time, indicating zero order reaction kinetics at constant oxygen and ammonia concentrations. Reaction rates were calculated from the slopes of these plots, and were generally found to be reproducible to within ± 5 per cent in duplicate experiments.

The only reaction products observed were $\text{Cu}(\text{NH}_3)_4^{++}$ and OH^- ions, in agreement with equation (1). No intermediate oxidation-reduction

³ Cupric ions exist predominantly as the tetrammine complex, $\text{Cu}(\text{NH}_3)_4^{++}$ in solutions containing NH₃ in excess of 10^{-2} m/l [see References (5) and (6)].

products such as peroxide or cuprous ions could be detected in the solution. With NH_3 concentrations in excess of 0.2 mole/l and at temperatures below 40°C , there was no indication of the formation of insoluble copper oxides or salts on the copper surface.

Effect of Surface Area and Solution Volume

Measurements of the effect of apparent surface area of the copper and of the volume of solution on the rate of dissolution are summarized in Table I. They show the total rate of dissolution (mg Cu/hr) to be independent of the volume and directly proportional to the surface area. This indicates that the rate-controlling step of the reaction occurs at the copper surface rather than homogeneously in the solution. All the kinetic results in this paper are expressed as specific rates (mg Cu/cm²/hr) and are thus independent of both the solution volume and copper surface area.

TABLE I. Effect of surface area and solution volume on the rate of dissolution of copper

Temp: 26°C ; solution: NH_3 —0.5 mole/l; O_2 partial pressure: 7.8 atm; stirring velocity: 660 rpm.

Surface area of Cu cm ²	Solution volume liters	Rate of dissolution of copper		Specific rate mg/cm ² /hr
		mg/l/hr	mg/hr	
2.0	2.0	27.5	55.0	27.5
2.0	3.0	20.0	60.0	30.0
2.0	4.0	13.5	54.0	27.0
2.0	5.0	13.8	64.0	32.0
4.0	3.0	40.5	121.5	30.4
Avg rate				29.4

The fact that zero order reaction plots were always obtained indicates that the surface area of the copper remains substantially constant during each experiment. Otherwise, a change in the rate corresponding to a deviation from the linearity of the rate plot would be observed.

Effect of Oxygen

Rate curves showing the effect of varying the oxygen pressure and the concentration of ammonia, respectively, on the dissolution of copper, are shown in Fig. 2 and 3. The variations are summarized in Fig. 4 where the rates at different ammonia concentrations are plotted as functions of the oxygen pressure. No dissolution of copper occurred in the absence of oxygen. At low oxygen pressures, the rate is directly proportional to the pressure, and independent of the ammonia concentration. This is taken as indicating that in this region (referred to subsequently as the region of low oxygen pressure) the rate is determined by the transport of oxygen to the copper surface (denoted by the broken line in

Fig. 4). As the pressure is increased, a point is reached where the rate becomes independent of oxygen pressure and levels off at a value which

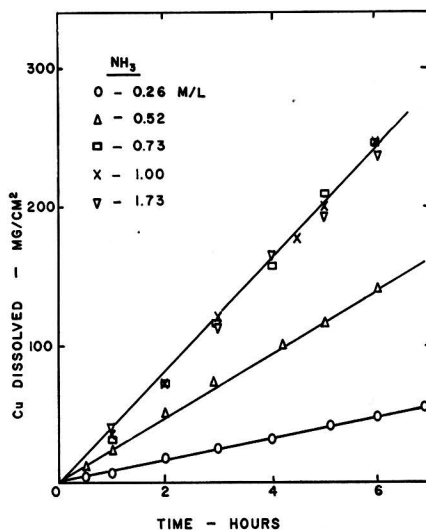


Fig. 3. Rate curves for the dissolution of copper in ammonia solutions. Effect of total NH_3 concentration. O_2 pressure, 3.0 atm; temperature, 26°C ; stirrer velocity, 660 rpm.

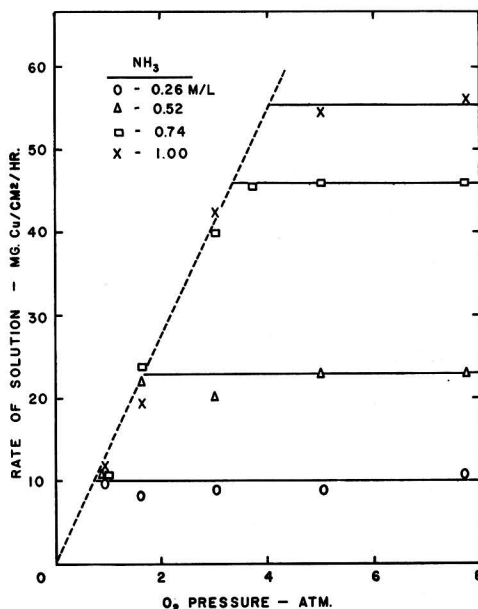


Fig. 4. Effect of oxygen pressure on the rate of dissolution of copper. Temperature, 26°C ; stirrer velocity, 660 rpm.

depends on the concentration of NH_3 . In this region (of high oxygen pressure), it appears that the concentration of oxygen and, consequently, its rate of

transport to the surface of the copper are sufficiently high that the rate of dissolution becomes controlled by the chemical reaction at the surface. The rate of this reaction appears to be independent of the concentration of oxygen. Its dependence on the concentration of ammonia will be discussed later.

These results, showing two distinct regions, corresponding to different apparent reaction orders with respect to the concentrations of oxygen and ammonia, indicate how the discrepancies in the reaction orders reported by different earlier investigators might have arisen.

Effect of Stirring Velocity

These conclusions about the significance of the two oxygen pressure regions are borne out by the results listed in Table II, showing how the stirring velocity influences the rate of dissolution in each region.

It is seen that in the low oxygen pressure region, the rate increases markedly with stirring velocity, characteristic of diffusion- or transport-controlled

TABLE II. Effect of stirring velocity on rate of dissolution
Temp: 26°C; solution: NH_3 —0.5 mole/l.

Stirrer velocity rpm	Specific rate of dissolution mg Cu/cm ² /hr	
	Low pressure region (O_2 = 1.4 atm)	High pressure region (O_2 = 7.8 atm)
470	15.0	30.0
545	17.6	29.0
660	19.3	30.0
820	21.6	31.9

reactions, whereas at higher oxygen pressures practically no dependence of the rate on stirring velocity is evident.

Effect of Temperature

Similar evidence is provided by the Arrhenius plots in Fig. 5, showing how the rate in each pressure region depends on the temperature. At low oxygen pressures, the activation energy was found to be 1330 cal/mole. Values of this low order are generally considered to indicate a diffusion- or transport-controlled rate (7). At higher oxygen pressures, the activation energy is 5540 cal/mole. This value, while still unusually low, is more consistent with a rate process-controlled by a chemical⁴ reaction. Activation energies as low as this are rarely observed for chemically controlled dissolution reactions, since they correspond to very fast reactions; the rate would therefore tend to be determined by slower transport processes. It was only by using elevated

⁴ The term "chemical" is used loosely here to include such processes as adsorption and desorption.

oxygen pressures in the present study that freedom from transport control could be achieved and the rate and activation energy, corresponding to the chemical reaction, measured.

All the kinetic results subsequently described in this paper were obtained in the region of high oxygen pressure and may consequently be taken as representing the chemical reaction, uninfluenced by the transport of reactants to the surface. The volume

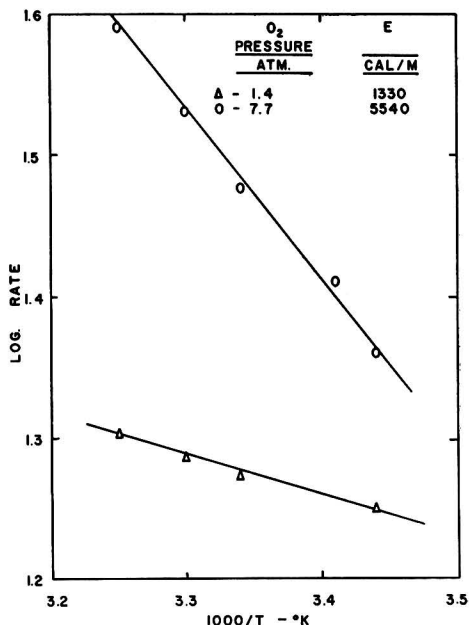


FIG. 5. Arrhenius plots for the dissolution of copper in aqueous ammonia. Total NH_3 , 0.5 mole/l; stirrer velocity, 660 rpm.

of solution in all experiments was 3 liters and the stirring velocity 660 rpm.

Effect of $\text{Cu}(\text{NH}_3)_4^{++}$

The fact that zero order reaction kinetics were always observed indicates that the copper dissolved during the reaction, mainly as $\text{Cu}(\text{NH}_3)_4^{++}$ ions, does not influence the rate. This was confirmed in an experiment in which 2.8×10^{-3} moles/l of CuSO_4 were added to the ammonia solution. The rate of dissolution was the same as when no copper was present initially in the solution.

Effect of Total Ammonia Concentration

Plots of the rate of dissolution of copper at 18° and 26°C, as functions of total NH_3 concentration, are shown in Fig. 6. In the absence of any added salts, the curves are seen to be S-shaped, indicating a complex relation. This is not surprising since

changes in the concentration of ammonia are always accompanied by simultaneous variations in the pH and ionic strength of the solution as well as in the concentrations of NH_4^+ and undissociated NH_3 . This is due to the ionization of ammonia, represented by the following equilibrium:



$$\frac{(\text{NH}_4^+)(\text{OH}^-)}{(\text{NH}_3)_{\text{aq}}} = K \quad (\text{III})$$

$$= 1.8 \times 10^{-5} \text{ at } 25^\circ\text{C}$$

In the experiments described subsequently, an attempt was made to investigate each of these variables separately.

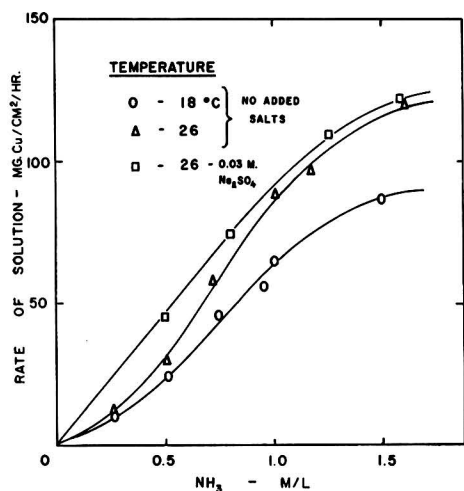


Fig. 6. Effect of total NH_3 concentration on the rate of solution of copper. O_2 pressure, 7.8 atm.

Effect of Electrolyte Concentration

At constant NH_3 concentration, the rate of dissolution of copper was found to increase on addition to the solution of an inert electrolyte such as Na_2SO_4 , as shown in Fig. 7. This does not appear to be due to a primary salt effect (8) since the relation between log rate and the square root of the ionic strength is not linear. Instead, the effect is seen to be most pronounced at low electrolyte concentrations with the rate levelling off as the amount of electrolyte is increased.

This electrolyte effect would account for the S-shaped character of the plots of rate against ammonia concentration in Fig. 6. On increasing the concentration of ammonia, the rate would be influenced by the change in the concentration of electrolyte (arising from the dissociation of NH_3) as well as by the change in the concentration of NH_3 itself. The former effect would be particularly pro-

nounced at low electrolyte (i.e., low ammonia) concentrations, accounting for the increasing slope of the initial part of the curve.

This was confirmed by measuring the change in rate with ammonia concentration in the presence of a constant excess concentration of Na_2SO_4 . Under these conditions, the initial portion of the plot, shown in the upper curve in Fig. 6, was found to be linear instead of S-shaped. The rate of dissolution thus appears to increase in an approximately linear manner, with the total ammonia concentration falling off slightly from the linear dependence at higher values. This fall off may be due to the rate

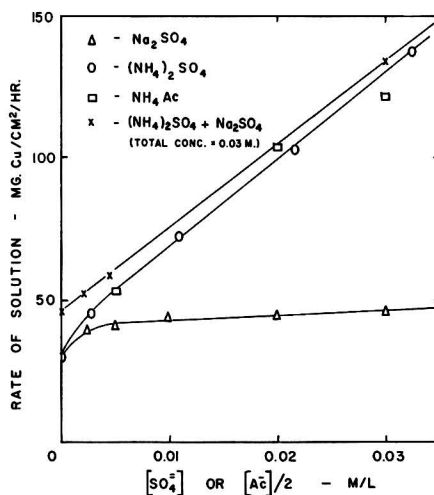


Fig. 7. Effect of various salts on the solution of copper in aqueous ammonia. NH_3 , 0.5 mole/l; O_2 pressure, 7.8 atm; temperature, 26°C .

becoming controlled in part by oxygen transport in the region of high NH_3 concentration.

Effect of NH_4^+

It remains to determine to what extent this apparently linear increase of the rate of dissolution with total NH_3 concentration is due to the NH_3 itself, and to what extent it is influenced by the accompanying increase in the concentrations of NH_4^+ and OH^- , arising from the ionization of NH_3 in accordance with equation (II). To obtain information on this point, a series of experiments was made in which the concentration of NH_3 was held constant and the concentration of NH_4^+ varied independently by adding different amounts of $(\text{NH}_4)_2\text{SO}_4$ or NH_4Ac to the solution. The variation of the rate with the concentration of these salts is plotted in Fig. 7.

Following an initial sharper rise, the rate of dissolution of copper is seen to increase in a linear manner with the concentration of $(\text{NH}_4)_2\text{SO}_4$.

Addition of ammonium acetate gave the same increase in rate as ammonium sulfate, whereas sodium sulfate gave only the initial increase. This shows that the subsequent linear increase of rate with ammonium salt concentration is due to the NH_4^+ ion. The initial sharper increase is due to the electrolyte effect discussed earlier. This is confirmed by the upper curve in Fig. 7, which shows that, when the electrolyte concentration was held constant by addition of Na_2SO_4 , the initial rise in this rate was not observed, and the increase of rate with the concentration of $(\text{NH}_4)_2\text{SO}_4$ was exactly linear over

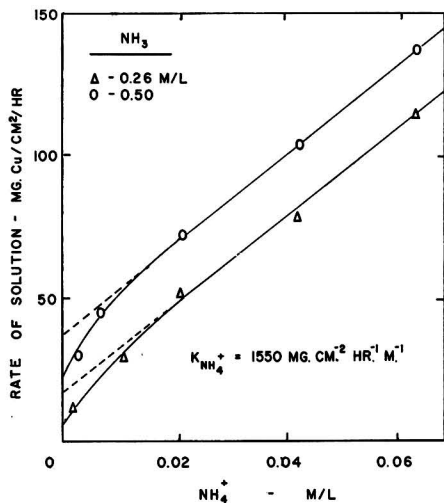


FIG. 8. Variation of the rate of solution of copper with the concentration of NH_4^+ . O_2 pressure, 7.8 atm; temperature, 26°C.

the entire range. The slope of the linear region was not appreciably altered.

Effect of H^+

Equation (III), representing the equilibrium for the ionization of ammonia, can be rewritten in the form:

$$\frac{(\text{NH}_4^+)}{(\text{H}^+)} \cdot \frac{1}{(\text{NH}_3)} = \frac{1.8 \times 10^{-5}}{Kw} \quad (\text{IV})$$

where Kw is the ion product of water = 10^{-14} at 25°C. Therefore

$$\frac{(\text{NH}_4^+)}{(\text{H}^+)} = 1.8 \times 10^9 (\text{NH}_3) \quad (\text{V})$$

This shows that at constant (NH_3) the concentration of H^+ in the solution is proportional to that of NH_4^+ , and any increase in (NH_4^+) is accompanied by a corresponding increase in (H^+) . The significance of the linear dependence of the rate on (NH_4^+) shown in Fig. 7 is therefore ambiguous, since it

could also be interpreted to signify a linear dependence on (H^+) .

To resolve this ambiguity, the variation of rate with ammonium sulfate concentration was measured at two different NH_3 concentrations. From equation (V), the ratio $(\text{NH}_4^+): (\text{H}^+)$ is proportional to (NH_3) and is, therefore, different for the two NH_3 concentrations. When the rate is plotted against (NH_4^+) , two parallel lines should be obtained if the increase in rate is due to NH_4^+ ions, whereas the two lines of different slope will be obtained if the rate increase is due to H^+ ions. Fig. 8 shows that the rates of dissolution vs. (NH_4^+) [the latter calculated from equation (V)] for (NH_3) values of 0.26 and 0.50 are, in fact, parallel.

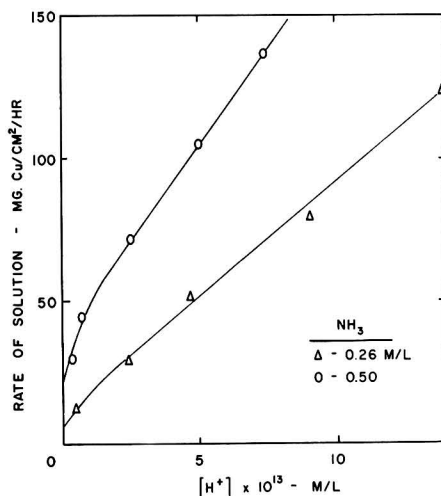


FIG. 9. Variation of the rate with the concentration of H^+ at different ammonia concentrations. O_2 pressure, 7.8 atm; temperature, 26°C.

On the other hand, the corresponding plots of rate against (H^+) in Fig. 9 have different slopes. This proves that the rate of dissolution increases linearly with the concentration of NH_4^+ , but does not depend directly on the concentration of H^+ .

Contributions of NH_3 and NH_4^+ to the Dissolution Reaction

The specific rate constant, $K_{\text{NH}_4^+}$, of the first order reaction due to NH_4^+ , can be calculated from the slopes of the linear portion of the plots in Fig. 8, and is found to have the value $1550 \text{ mg Cu/cm}^2/\text{hr}/(\text{NH}_4^+)$. Extrapolation to zero (NH_4^+) shows that this reaction accounts for only part of the dissolution rate. The remainder must be attributed to a separate reaction which appears to be due to undissociated NH_3 .

The relative contributions of the two reactions to

the total dissolution rate (R_T), for a series of ammonia solutions of varying concentration, but containing no added ammonium salts, are shown in Fig. 10. The contribution of the NH_4^+ reaction, ($R_{\text{NH}_4^+}$), was calculated from the specific rate constant determined above, i.e.,

$$R_{\text{NH}_4^+} = K_{\text{NH}_4^+}(\text{NH}_4^+) \quad (\text{VI})$$

where (NH_4^+) was calculated from equation (III).

The contribution of the NH_3 reaction, (R_{NH_3}), was taken as the difference between the total rate and $R_{\text{NH}_4^+}$, i.e.,

$$R_{\text{NH}_3} = R_T - R_{\text{NH}_4^+} \quad (\text{VII})$$

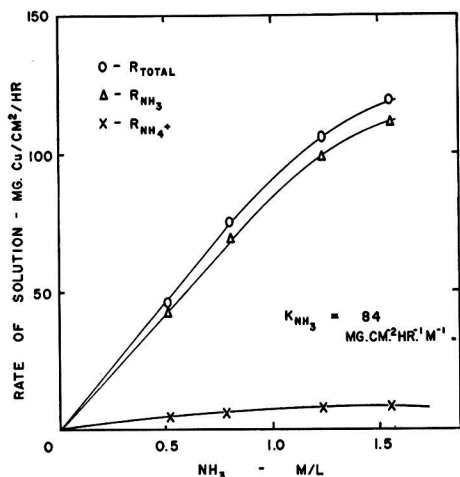


FIG. 10. Contributions of NH_3 and NH_4^+ to the total rate of dissolution of copper in aqueous ammonium solutions containing no added ammonium salts. Na_2SO_4 , 0.03 mole/l; O_2 pressure, 7.3 atm; temperature, 26°C .

The plot of R_{NH_3} against (NH_3) is also linear, at least in the initial region, indicating a first order reaction with respect to (NH_3) . As suggested earlier, the falling off in the rate at higher values, from the linear dependence, may be attributed to an oxygen deficiency under these conditions with consequent rate control by oxygen transport. The first order rate constant, K_{NH_3} , for the NH_3 reaction was calculated from the slope of the linear region and found to be $84 \text{ mg Cu/cm}^2/\text{hr}/(\text{NH}_3)$.

CONCLUSIONS

It has been shown that the total rate of dissolution of copper in ammonia solutions, in the presence of an excess of oxygen, is made up of the contributions of two separate reactions, apparently proceeding independently of each other. The rates of these two

reactions are first order with respect to the concentrations of NH_3 and NH_4^+ , respectively,

$$R_T = K_{\text{NH}_4^+}(\text{NH}_4^+) + K_{\text{NH}_3}(\text{NH}_3).$$

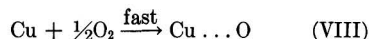
At a total electrolyte concentration equivalent to 0.03 mole/l of Na_2SO_4 , $K_{\text{NH}_4^+}$ and K_{NH_3} are equal to 1550 and $84 \text{ mg Cu/cm}^2/\text{hr}/\text{mole}$, respectively.

These values are dependent to a slight extent on the electrolyte concentration, particularly at low concentrations.

Both $K_{\text{NH}_4^+}$ and K_{NH_3} are independent of the pressure or concentration of oxygen, providing the latter is present in excess, so that its transport to the surface of the copper does not limit the reaction rate.

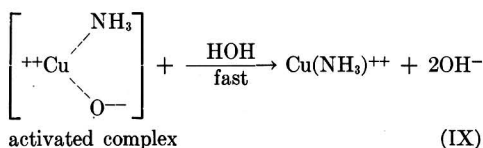
These kinetic results and the observed reaction products are consistent with a mechanism for the dissolution process, involving the following sequence of steps:

1. Adsorption of dissolved oxygen onto the copper surface:

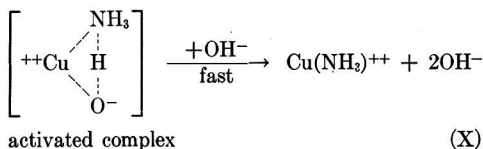


The fact that the rate of dissolution is independent of the concentration of oxygen indicates that this step is fast, and that the surface is always covered with a film of oxygen.

2. Reaction of an NH_3 molecule or NH_4^+ ion with the copper-oxygen complex on the surface:



or



The kinetic results suggest that the oxide film, which is formed initially, does not grow appreciably in thickness. Such growth is generally observed when copper is exposed to gaseous oxygen or to solutions of salts such as KCl containing oxygen, and leads to the formation of a stable layer of cuprous oxide. However, this does not appear to take place in the present system, i.e., when the copper is exposed to a solution containing ammonia and oxygen in excess,

under conditions where cuprous oxide is thermodynamically unstable. Instead it would appear that the film of adsorbed oxygen which forms initially is attacked by NH_3 or NH_4^+ , as shown above, and dissolves. This stage of the reaction is rate-determining, consistent with the observed first order dependence of the dissolution rates on the concentrations of NH_3 and NH_4^+ (as well as on the copper surface area). The two reactions proceed independently, both leading to the formation, in the first instance, of a $\text{Cu}(\text{NH}_3)_2^{++}$ ion. The copper probably dissolves in this form, reacting rapidly in solution with more NH_3 molecules to form higher amines, such as $\text{Cu}(\text{NH}_3)_4^{++}$, which are more stable.

While a detailed description of the activated complex or transition state for these reactions is impossible, reasonable structures which probably incorporate the essential features are suggested above in equations (IX) and (X). The formation of the activated complex must involve, in each case, the coordination of a NH_3 group to a Cu atom, accompanied by a transfer of electrons from the Cu to an adsorbed O atom, leading to the incipient formation of $\text{Cu}(\text{NH}_3)_2^{++}$ and O^{--} . Where the reactant is NH_4^+ , the activated state would be expected to have a lower energy than that resulting from reaction with NH_3 , since the extra proton in NH_4^+ would certainly act to stabilize the O^{--} (i.e., OH^- is formed instead of O^{--} , the latter being less stable), even if allowance is made for the fact that the activated complex is further stabilized through solvation by water. This is consistent with the experimental observation that the rate constant for the NH_4^+ reaction is considerably larger (by a factor of 18.5) than the rate constant for the NH_3 reaction.

An alternative possibility is that the copper dissolves initially, by a similar mechanism, as a cuprous complex ion, i.e., $\text{Cu}(\text{NH}_3)_2^+$, which is subsequently oxidized homogeneously in the solution to the cupric state. Since the latter reaction is fast, such a scheme would also be consistent with the observed reaction products and with the kinetic results described above. However, it is considered likely that in the presence of an excess of oxygen at the surface, such as was maintained in the present system, oxidation to the cupric state would occur at the surface, and the copper would dissolve in the first instance as a cupric ion. Some further support for this is provided by the fact that the reaction is not catalyzed by dissolved cupric salts. But whatever the identity

of the dissolving ion, there would appear to be little doubt about the essential features of the mechanism which involves the initial rapid formation of an oxide film and the subsequent rate-determining attack by NH_3 or NH_4^+ .

Such a mechanism appears to be consistent with all the kinetic results obtained in this investigation. It accounts for the first order dependence of the rate on the concentrations of NH_3 and NH_4^+ , for the relative orders of magnitude of the two rate constants, and for the fact that the rate is independent of the concentrations of H^+ , oxygen, and dissolved copper. Since the activated complex has the same net charge as the reactant species (NH_3 or NH_4^+), the absence of a large primary salt effect is also explained. The relatively small electrolyte effect which was observed appears to be of a secondary nature, and is probably related to changes in charge distribution accompanying the activation process or to the influence of ionic strength on the ionization of NH_3 . No attempt has been made to follow up its investigation in detail, and its exact significance is not clear.

The proposed mechanism is also consistent with general chemical and energetic considerations, and with measurements (9) which suggest that even at low temperatures, oxygen is chemisorbed rapidly on the surface of copper, so that the subsequent reaction with ammonia and water would be likely to constitute the slow step in the over-all process of formation and dissolution of the complex ion.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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The Quantitative Electrodeposition of Radium Ruthenium¹

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ABSTRACT

A study has been made to determine the conditions necessary for the complete (~99%) electrodeposition of rutherfordium. Bright adherent deposits suitable for small radioactive sources were obtained from acid solutions containing moderately low concentrations ($5 \times 10^{-3} - 5 \times 10^{-5}M$) of ruthenium nitroso salts. The minimum cathode potential at which complete deposition was possible was about -0.45 volt vs. S.C.E.

INTRODUCTION

Ruthenium is one of the most abundant elements formed during the process of nuclear fission. One of its radioisotopes, Ru¹⁰⁶, has radiation characteristics which may be of value where a high energy beta source is required, for example in radiation therapy. Ru¹⁰⁶ has a half-life of approximately one year, and decays to Rh¹⁰⁶, by the emission of a low energy beta particle. The half-life of Rh¹⁰⁶ is 30 sec, and the decay radiation consists largely of very energetic beta particles with a smaller fraction of gamma rays (1). As a result of the secular equilibrium existing between Ru¹⁰⁶ and Rh¹⁰⁶, the half-life of the high energy beta radiation can be considered to be one year.

Relatively large amounts of rutherfordium are obtainable through the Radioisotopes Sales Department of Oak Ridge National Laboratory. The available supply is usually in the form of a solution containing between 50 and 100 parts per million of ruthenium. The specific activity of the ruthenium is in the order of 20 millicuries/mg of ruthenium.

In view of the radiation characteristics and availability of Ru¹⁰⁶, it was desirable to have a method of concentrating the rutherfordium so that it could be used efficiently in relatively small radiation sources. Electrodeposition appeared to offer the best means of preparing compact sources of rutherfordium, particularly in view of the fact that, by this method, the ruthenium could be deposited on cathodes of the shape best suited for the intended use. Therefore, an investigation of the possibility of electroplating ruthenium from dilute solutions was undertaken.

The electrodeposition of ruthenium for ornamental or protective purposes has been successfully carried out under a number of different conditions. In a

series of patents (2), numerous ruthenium plating baths have been described and in all of them the ruthenium was present either as the nitroso or as the nitrosoammino salt. The plating baths contained one to two grams of ruthenium per liter and were operable over a wide range of pH values. However, the above patents do not describe conditions necessary to obtain a smooth, adherent deposit when the ruthenium concentration is low, nor do they give the conditions necessary for essentially complete removal of ruthenium from solution.

The present paper presents a convenient method for converting the rutherfordium available at Oak Ridge National Laboratory to the nitroso salt, and its subsequent electrodeposition. For a method to be suitable the following three requirements had to be considered: (a) a minimum of complex operations in the preparation of the electrolyte; (b) essentially complete removal of ruthenium from solution; and (c) a compact and adherent deposit. Since in the future it may be desirable to separate ruthenium from other reducible ions, perhaps other fission products, the cathode potential needed to obtain complete deposition was also determined.

EXPERIMENTAL

Procedure

All electrolyses were carried out in a cell of the type previously described (3). In general, the cell assembly consisted of a brass stand on which a foil cathode rested. A glass cylinder was clamped on the foil cathode, the exposed area of which was 5 cm².

A constant cathode potential regulator of the type described by Lamphere (4) was used as the power source. The anode and reference electrode, a saturated calomel electrode (S.C.E.), were placed in separate vessels and connected to the electrolysis cell by means of bridges containing tight filter-paper plugs in the ends, in contact with the plating solution. The bridges were filled with either 6*N* hydrochloric or sulfuric acid. The outside anode was used to prevent possible oxidation of the ruthenium to the

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volatile tetroxide and/or deposition of the dioxide on the anode.

The voltage regulator and the described electrolysis cell were not essential for the successful electro-deposition of ruthenium. However, the regulator did permit a determination of the deposition characteristics of ruthenium, and the cell confined the cathode deposit to an area which could be counted easily with a standard Geiger-Müller counter.

Since direct use of the rutheruthenium solutions available at the laboratory would have required excessive shielding, a natural ruthenium solution, to which only a trace of rutheruthenium had been added, was used. A normal ruthenium stock solution was prepared by dissolving sufficient ruthenium chloride (J. Bishop & Company) in 6*N* hydrochloric acid to form a 0.1*M* solution. All ruthenium plating solutions were prepared from dilutions of this solution.

To convert the normal ruthenium solution to the nitroso species, a solution of ruthenium chloride, to which a small amount of tracer had been added, was evaporated to near dryness under a heat lamp. Then a small amount (usually 2 to 3 ml) of red fuming nitric acid (sp gr = 1.60) was added and the resulting solution was taken to near dryness. A second addition of red fuming nitric acid was made, and the solution was evaporated to dryness. The residue was dissolved in a few drops of concentrated hydrochloric acid and taken to dryness to reduce the nitrate ion concentration to a very low value. The residue was then dissolved in the electrolyte from which the ruthenium was to be deposited. When nitric acid was to be the supporting electrolyte, the treatment with hydrochloric acid was omitted. If the supporting electrolyte was to be sulfuric acid, a drop of concentrated sulfuric acid was added and the solution was slowly fumed for a few minutes. All solutions were prepared with reagent grade chemicals and distilled water.

The general procedure was to electrolyze a 20-ml aliquot of a solution for a given period of time. During the electrolysis, the electrolyte was stirred with a motor-driven single-blade glass stirrer. Most of the electrolyses were carried out at room temperature (about 25°C), using a copper foil cathode. In one series of experiments, nickel, gold, and platinum foils were used as cathodes and a few electrolyses were performed at 100°C. All cathodes were first cleaned in a hot, concentrated alkali solution, dipped in dilute hydrochloric acid, and then rinsed in distilled water. In order to determine the amount of ruthenium remaining in solution at any given time, a 0.100-ml aliquot was pipetted from the cell without interrupting the electrolysis. The aliquot was then evaporated to dryness on a 1-in. watch glass, mounted in an aluminum card, and counted. At

the completion of an electrolysis, the cathode was removed from the cell and counted. All counts were corrected for coincidence, size of aliquot, difference in back scattering, and counter geometry. Decay corrections were unnecessary since all counts were compared with a sample of the original solution counted at the same time.

Completeness and Rate of Deposition

Preliminary experiments were carried out to find an electrolyte from which at least nearly complete ruthenium deposition could be obtained. For this study, the ruthenium concentration was $5 \times 10^{-4}M$ and the ruthenium had not been converted to the nitroso complex. Solutions of ruthenium chloride in either hydrochloric, sulfuric, or nitric acid at acid concentrations of 0.1 and 0.3*N* were electrolyzed at cathode potentials as high as -1.5 volts vs. S.C.E. In no case was more than 80 per cent of the ruthenium deposited, even after prolonged electrolysis. All of the deposits were black and nonadherent, and the amount plated in any of the above systems was not reproducible. Attempts to obtain complete plating from solutions of ammonia, potassium cyanide, or the sodium salt of ethylene diamine tetracetic acid were likewise unsuccessful.

When a ruthenium nitroso salt was substituted for the normal ruthenium salt in either sulfuric or hydrochloric acid, an electrolyte was obtained from which complete plating was possible at cathode potentials as low as -0.45 volt vs. S.C.E. Fig. 1 shows the rate and completeness of plating in the described cell when the supporting electrolyte was $5 \times 10^{-4}M$ in the appropriate ruthenium nitroso salt and 0.3*N* in either hydrochloric, sulfuric, or nitric acid. In each case, the solutions were electrolyzed at room temperature at a cathode potential of -0.60 volt vs. S.C.E., using copper cathodes. If the nitric acid used in the preparation of the nitroso compound was not completely removed, or if the supporting electrolyte was nitric acid, no more than 80 per cent of the ruthenium could be deposited at cathode potentials of -1.00 volt vs. S.C.E. In a few cases where the electrolyses in hydrochloric or sulfuric acid were continued for five hours, as much as 99.7 per cent of the ruthenium was deposited. Changing the acid concentration in the supporting electrolyte to 0.1*N* did not produce a noticeable change in either the rate of plating or in the appearance of the deposit.

The deposits obtained from the above baths were excellent, particularly those obtained from hydrochloric and sulfuric acid solutions. Those prepared in either sulfuric or hydrochloric acid solutions were silvery-white and lustrous; those prepared from nitric acid solutions were also lustrous, but slightly

darker. The adherence of the deposits from all baths was very good. In all cases, it was possible to bend the cathode through 180° without any evidence of the deposit peeling from the cathode. On repeated bending, small amounts of ruthenium did peel from the cathodes prepared in nitric acid, while under the same conditions the deposits prepared in sulfuric or hydrochloric acid showed no tendency to peel. In fact, on repeated bending, the foil usually broke without any evidence of the ruthenium being separated from the base metal.

Since the deposits obtained by completely depositing ruthenium from $5 \times 10^{-4}M$ ruthenium nitroso

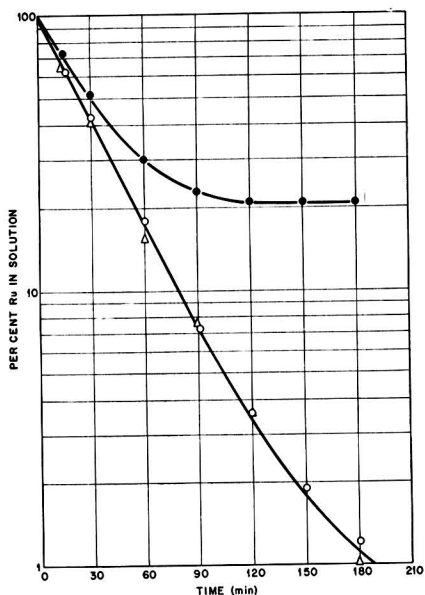


FIG. 1. The rate of plating from $5 \times 10^{-4}M$ RuNOCl_2 in different acid solutions. \circ — $0.3N$ HCl ; \triangle — $0.3N$ H_2SO_4 ; \bullet — $0.3N$ HNO_3 .

salt solutions in either sulfuric or hydrochloric acid at room temperature were so good, only one deposit was prepared from each of the above electrolytes at 100°C . In both cases there was no apparent improvement of the deposit, although the rate of plating was greatly increased. For example, at room temperature, 99 per cent deposition required approximately three hours; at 100°C , the same amount was deposited in one hour. Because of the difficulty of removing metallic ruthenium from the cathode, nearly all of the electrolyses were performed with copper cathodes which were discarded at the completion of an experiment. However, one series of experiments was run using platinum, gold, and nickel cathodes, and their use produced no apparent change

in either the rate of plating or the appearance of the deposit.

When the initial ruthenium concentration was decreased to $5 \times 10^{-5}M$, the rate of deposition was not changed, but only about 95 per cent of the ruthenium could be deposited at 25°C . At this concentration, the amount of ruthenium deposited on the cathode was so small (0.02 mg/cm^2) that it appeared dark. The adherence was good, as shown by the fact that it was impossible to remove a detectable

TABLE I. The amount of ruthenium deposited from $5 \times 10^{-4}M$ RuNOCl_2 in $0.3N$ HCl at various cathode potentials at 3 and 5-hr intervals

Cathode potential vs. S.C.E.	% Ru deposited 3 hr	% Ru deposited 5 hr	Material balance %
-0.40	96	99	101
-0.30	89	93	101
-0.25	76	85	102
-0.23	71	73	97
-0.20	21	32	99
-0.15	<1	9	98

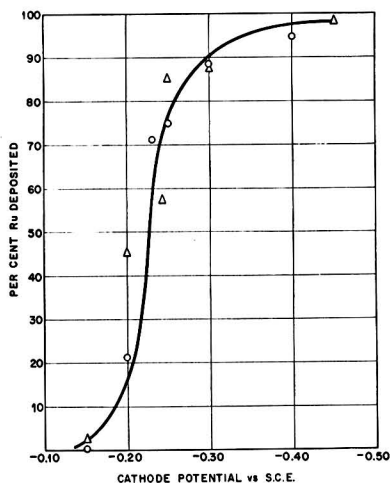


FIG. 2. The deposition curve for $5 \times 10^{-4}M$ RuNOCl_2 . \circ — $0.3N$ HCl supporting electrolyte; \triangle — $0.3N$ H_2SO_4 supporting electrolyte.

amount from the surface by rubbing with coarse filter paper.

Reducing the initial ruthenium concentration to $5 \times 10^{-6}M$ or less always resulted in no more than 80 per cent of the ruthenium being deposited, even at cathode potentials as high as -1.2 volts vs. S.C.E. A later paper (5) presents a thorough study of ruthenium deposition from extremely dilute solutions.

The highest concentration of ruthenium nitroso chloride from which plating was attempted was $5 \times$

$10^{-3}M$. In one run at room temperature where the electrolyte was $5 \times 10^{-3}M$ ruthenium nitroso chloride in $0.3N$ hydrochloric acid and the cathode potential was -0.60 volt vs. S.C.E., only 81 per cent of the ruthenium was plated after five hours. Although the ruthenium was still depositing at a slow rate, the cathode was black and spongy. In another run where the conditions were identical to the first, except that the cell was placed in a boiling water bath, the rate was greatly accelerated and in one hour 97 per cent of the ruthenium was deposited. Under the latter conditions, the cathode deposit was uniformly bright, and its adherence to the copper cathode was equal to that of the thinner deposits.

Deposition Potential

The cathode potential needed to deposit ruthenium from the ruthenium nitroso salt was determined at room temperature under two conditions: $5 \times 10^{-4}M$ ruthenium nitroso sulfate in $0.3N$ sulfuric acid; and $5 \times 10^{-4}M$ ruthenium nitroso chloride in $0.3N$ hydrochloric acid. In each case, six electrolyses were carried out at potentials between -0.15 volt and -0.45 volt vs. S.C.E. for three hours, a time of electrolysis sufficient to allow substantially complete deposition at -0.60 volt vs. S.C.E. At the completion of the three-hour electrolyses in hydrochloric acid solutions, duplicate aliquots were withdrawn to determine the amount plated. Then the electrolyses were continued for an additional two hours, at the end of which time the cathodes were removed and counted. Table I shows the amount plated at the end of each time as well as the material balances obtained. In most cases, a small amount of ruthenium was deposited during the final two-hour period, but the amount was not sufficient to appreciably change the shape of the deposition curve.

The electrolyses carried out in sulfuric acid solution were continued for only three hours, at the end of which time duplicate aliquots of the solution and the cathode were counted. Fig. 2 shows the amount of ruthenium plated at each potential in both sulfuric and hydrochloric acid solutions after three hours. It is apparent that the deposition characteristics of the two systems were quite similar and that essentially complete deposition was obtained at -0.45 volt vs. S.C.E.

DISCUSSION

The method of preparing the nitroso compound presented in this paper is perhaps the simplest method for preparing the nitroso salts in small quantities. Attempts to prepare the same salt by heating a normal ruthenium salt with concentrated nitric acid or with aqua regia did not yield a salt from which the ruthenium could be deposited in a suit-

able form. That the nitroso compound was not formed in substantial amounts by either of the latter two treatments was evidenced by the color of the solutions. Dilute solutions of the ruthenium nitroso chloride are wine-red, while those prepared from the product formed by heating with either aqua regia or concentrated nitric acid were dark brown, the same as the normal salts. It appeared that the nitrogen dioxide dissolved in the red fuming nitric acid was responsible for the conversion to the nitroso form; later work has verified this observation (5). The solutions of ruthenium nitroso sulfate were not as red as those of the chloride, but were reddish brown. However, there appeared to be no difference in the plating characteristics of the two solutions.

The acid concentration of the supporting electrolyte did not appear to be critical. Good deposits were obtained at $0.1N$ and $0.3N$, and some experiments of a qualitative nature indicated that equally good deposits could be obtained at considerably higher concentrations. At the cathode potentials used, hydrogen ion concentrations greater than approximately $0.3N$ caused excessive currents due to hydrogen evolution. When the total current through the anode salt bridge became greater than about 0.15 amp, the heat produced in the bridge caused bubbles, which broke the circuit.

At an acid concentration of $0.3N$ a cathode potential of -0.40 volt vs. S.C.E. corresponded to a current density of 1.0 amp/dm², while a cathode potential of -0.60 volt vs. S.C.E. corresponded to approximately 3.0 amp/dm². Hence, good deposits were obtained between 1.0 and 3.0 amp/dm².

That the electrochemical properties of the inactive ruthenium used throughout these experiments did not differ appreciably from those of radioruthenium was evidenced by the fact that the Development Department of the Operation Division of the laboratory has prepared several radioruthenium plates ranging in activity from 10 to 125 millicuries using the general method given in this paper (6). The deposition characteristics and the appearance of the deposits seemed to be the same as those prepared with inactive ruthenium. The smoothness and adherence of the deposits were such that no difficulty was encountered in depositing a thin protective layer of silver over the surface of the radioactive ruthenium.

The deposition potential of ruthenium as determined was purely empirical in nature and no effort was made to minimize or correct for junction potentials. It is interesting to note that at a reasonably low cathode potential, -0.45 volt vs. S.C.E., essentially complete deposition was obtained. Under the conditions used it was impossible to determine

whether or not the deposition of ruthenium could be completely prevented at cathode potentials more noble than -0.15 volt vs. S.C.E. because of the reactivity of the copper cathodes. However, the data would seem to indicate that ruthenium could be separated from some noble metals and from certain of the more active metals by the use of a controlled cathode potential technique.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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A Study of the Electrodeposition of Ruthenium from Very Dilute Solutions¹

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ABSTRACT

The deposition behavior of ruthenium at low concentrations has been investigated under a variety of conditions. Only when the ruthenium was in solution as the ruthenium nitroso complex were reproducible results obtained. Complete deposition was not possible at concentrations below 10^{-5} molar. A mechanism involving a catalytic hydrogen reduction of the ruthenium nitroso complex is proposed to account for the complete deposition of macro amounts of ruthenium and the incomplete deposition of micro amounts.

INTRODUCTION

A previous paper has shown that essentially complete deposition of ruthenium was possible if the concentration of ruthenium in solution was $5 \times 10^{-5}M$ or greater (1). When the initial concentration of ruthenium was less than $5 \times 10^{-6}M$, the deposition was never complete, even after prolonged electrolysis.

The present investigation was undertaken to determine, in general, what variables affect the electrodeposition of ruthenium from its nitroso salts and, in particular, to study the deposition process from very dilute solutions. Since numerous studies (2-5) have been carried out using trace concentrations of other elements, most of which behave nearly reversibly, it was of interest to see how a strictly irreversible deposition compared with the reversible ones. In addition, such a study might be of value in attempting to separate ruthenium from other fission products.

EXPERIMENTAL DETAILS

The electrolysis cell, the electrode arrangement, the regulator for the control of the cathode potential, and the method of determining the amount plated were the same as those described in the previous paper (1). The volume of solution electrolyzed was 10 ml in each case, and the solutions were stirred rapidly during electrolysis. Most electrolyses were performed at room temperature (about 25°C), but in a few cases where careful control of the temperature was necessary a constant temperature bath controlled to $\pm 0.5^\circ C$ was used.

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A number of different metals was used as cathodes. Since it was necessary to remove the ruthenium from the surface of the gold and platinum electrodes and reuse them, these electrodes were cleaned by making them the anode in a strong sodium cyanide solution. With the platinum electrodes, a current of 10 amp was passed for one minute (1-2 amp/in.²); with the gold electrodes, a lower current was passed for a shorter length of time. All new electrodes were also given the above treatment before use. No other treatment seemed to be as satisfactory for removing ruthenium, and it appeared that this method was effective because the slow dissolution of the base metal swept the ruthenium from its surface. After the cathodes were removed from the cyanide solution, rinsed with distilled water, and dried, they were ready for use.

The copper cathodes were degreased in trichloroethylene, rinsed in acetone, dipped in dilute hydrochloric acid, rinsed in distilled water, and then dried. Each copper cathode was used once and then discarded.

Since 1-mil foil was used in the case of rhodium, palladium, and tantalum, each cathode was used only once. The cathodes were washed in trichloroethylene, thoroughly rinsed in acetone, and dried in air.

When platinum black electrodes were to be used, the cell was assembled in the usual fashion, with a clean platinum foil as cathode. Then 20 ml of a 3 per cent chloroplatinic acid solution was added and a platinum anode inserted. The solution was electrolyzed for 30 min at 0.015-0.02 amp/cm². After this time the solution was removed and the cell very thoroughly rinsed with distilled water. The solution to be electrolyzed was then introduced into the cell and the electrolysis performed. The cathode was not allowed to become dry after the washing process.

Even with the most dilute solutions used, adsorption of ruthenium was no problem, and material balances of 98–100 per cent were nearly always obtained. When the material balance was less than 95 per cent, the result was discarded and the experiment was repeated.

Preparation of Ruthenium Nitroso Salts

Preliminary experiments confirmed the observation that plating from the nitroso compound was necessary for obtaining satisfactory deposition of ruthenium. (In fact, from a very dilute solution of ruthenium chloride $5 \times 10^{-8}M$ in 0.1M hydrochloric acid, no ruthenium was deposited at cathode potentials as high as -1.20 volt vs. S.C.E.) Therefore, in all of the experiments described in this paper, the ruthenium nitroso salts were used. In preparing the plating solutions, ruthenium tracer (plus inactive ruthenium chloride for the higher concentrations) was converted to the nitroso form with red fuming nitric acid in the manner already described (1).

Since some uncertainty existed about the composition of the ruthenium salt prepared with the red fuming nitric acid, it seemed advisable to prepare a large enough quantity of ruthenium nitroso chloride so that an analysis could be made to check the empirical formula of the compound. Since ordinary nitric acid did not effect the conversion, it appeared that it was the nitrogen dioxide in the red fuming nitric acid that converted the ruthenium to the nitroso form. Therefore, the compound analyzed was prepared by bubbling nitrogen dioxide gas through a concentrated ruthenium chloride solution. During the reaction, the color of the solution changed to the wine-red color characteristic of ruthenium nitroso chloride. After the treatment with nitrogen dioxide, the solution was evaporated to a small volume several times with concentrated hydrochloric acid to remove excess oxides of nitrogen. Then the solution was evaporated in vacuo at room temperature. The dry ruthenium nitroso chloride crystals prepared in this way were very deliquescent and were stored in vacuo over anhydrous. According to Gmelin's Handbuch (6), ruthenium nitroso chloride recovered from solution at room temperature has the formula $RuNOCl_3 \cdot 5H_2O$. The analytical values actually obtained and the theoretical values based on the formula $RuNOCl_3 \cdot 5H_2O$ checked very closely. Hence it appeared certain that the empirical formula of the ruthenium compound used in the experiments described below was $RuNOCl_3 \cdot 5H_2O$.

EXPERIMENTAL RESULTS

Completeness of Plating

Since a previous paper had indicated that the amount of ruthenium that could be deposited from

a solution of ruthenium nitroso chloride was related to the initial ruthenium concentration, a large number of electrolyses (at least six at each concentration) were performed in which all conditions were kept constant except the initial ruthenium concentration. For these studies, the supporting electrolyte was 0.3M hydrochloric acid at room temperature, and the cathode potential was maintained constant at -0.60 volt vs. S.C.E. In all cases, freshly prepared solutions were used. For the electrolyses at concentrations greater than $5 \times 10^{-6}M$, copper cathodes were used; for those runs using a concentration of $5 \times 10^{-6}M$ or less, platinum electrodes were used. Reproducible results were not obtainable from the dilute solutions with copper cathodes. Since preliminary experiments had indicated that after 90 min practically no further deposition occurred, all electrolyses were continued for two hours to insure complete deposition. The amount of ruthenium that could be plated from the different solutions is shown in Table I. It should be noted that at ruthenium

TABLE I. Amount of ruthenium deposited from $RuNOCl_3$ solutions of various concentrations at a cathode potential of -0.60 volt vs. S.C.E.

Initial ruthenium concentration	% Ruthenium deposited
$5 \times 10^{-4}M$	99
$5 \times 10^{-5}M$	96–97
$5 \times 10^{-6}M$	79–83
$5 \times 10^{-7}M$	79–83
$5 \times 10^{-8}M$	79–83

concentrations greater than $5 \times 10^{-6}M$ essentially complete deposition was possible, while at concentrations $5 \times 10^{-6}M$ or less only about 80 per cent of the ruthenium was deposited.

Attempts were made to obtain complete deposition at the lower ruthenium concentrations by increasing the time of electrolysis to as long as eight hours and by increasing the cathode potential to -1.00 volt vs. S.C.E. Even under these extreme conditions, no additional ruthenium was deposited. Decreasing the acid concentration of the supporting electrolyte to 0.01M likewise did not change the per cent plated. The same amount of ruthenium was also deposited at $100^\circ C$, but at this temperature the rate of deposition was much faster than at room temperature. The same per cent of ruthenium remained in solution at the lower concentrations whether the solutions were prepared directly (with red fuming nitric acid) or by dilution of a more concentrated solution from which complete plating was possible.

When the solution remaining after electrolysis of a very dilute solution ($5 \times 10^{-6}M$ or less) was pipetted from the cell and placed in another cell

containing a new cathode, no additional ruthenium could be deposited. However, when this same solution was evaporated to dryness, treated again with red fuming nitric acid, the residue dissolved in hydrochloric acid, and the solution diluted to the same volume as before, the ruthenium could again be deposited to about the same fractional extent as it could from the original solution.

The fact that ruthenium could be nearly completely deposited from 5×10^{-4} and $5 \times 10^{-5}M$ solutions and only about 80 per cent deposited from the more dilute solutions appeared to indicate that, if enough ruthenium were present in solution to form at least several layers of ruthenium atoms on the surface, essentially complete deposition was possible. On the other hand, if only sufficient ruthenium were present to form less than a few atomic layers, deposition was incomplete. The atomic radius of a ruthenium atom is $1.32 \times 10^{-8}cm$; if one assumes uniform covering of the cathode with the deposited ruthenium, it can be shown that the surface area of the cathode occupied by the ruthenium atoms in 10 ml of a $5 \times 10^{-5}M$ solution is equal to $164 cm^2$, which would correspond to a deposit 33 atoms thick on the basis of a $5\text{-}cm^2$ plane surface area for the cathode. In the case of a $5 \times 10^{-6}M$ solution, this would correspond to only 3.3 atomic layers. In view of the cleaning which the cathodes had undergone, the true surface area of the cathodes was probably considerably greater than that of the plane area. Hence, using the plane area of the cathode and assuming uniform deposition, it appeared that a ruthenium deposit of approximately 30 atomic layers was necessary to insure complete plating.

Effect of Cathode Area

The above data indicated that, if sufficient ruthenium were plated to form a layer of ruthenium on the cathode several atoms thick, substantially complete ruthenium deposition was possible. On the basis of this observation, two electrolyses were carried out using, in one case, a plane electrode area of $5 cm^2$ and, in the other, an area of $0.05 cm^2$. Both runs were made at a potential of -0.60 volt vs. S.C.E. with 10-ml aliquots of a $10^{-6}M$ ruthenium nitroso chloride solution in $0.1M$ hydrochloric acid. In the case of the $5\text{-}cm^2$ cathode there was insufficient ruthenium in solution even with complete deposition to form a monolayer of ruthenium atoms on the cathode. In case of the smaller cathode, there was enough ruthenium in solution so that, if it were completely and uniformly deposited, the ruthenium would have been approximately 70 atomic layers thick.

Only 66 per cent of the ruthenium could be deposited on the cathode of $5\text{-}cm^2$ area. (The solution

had aged for about three weeks; see later section.) A much higher per cent of ruthenium was deposited on the small cathode, but the rate of deposition was extremely slow. After 65 hours, 87 per cent of the ruthenium had been deposited. Although the ruthenium may have still been depositing at a very slow rate, the electrolysis was discontinued. While the results of this experiment were not as conclusive as they might have been, they clearly show that the extent of deposition was greater on the small cathode.

Age of the Solution

After some time, it became apparent that the very dilute solutions changed with age: after standing for several days, less ruthenium could be deposited than when the solutions were freshly prepared. For example, 79 per cent of the ruthenium could be deposited from a freshly prepared $5 \times 10^{-6}M$ ruthenium nitroso chloride solution, but only 48 per cent of the ruthenium could be plated after 41 days.

While the amount of ruthenium that could be deposited from a $5 \times 10^{-4}M$ ruthenium nitroso chloride solution did not change with time, the solution itself did undergo change as shown by the following experiment. Three days after preparing a $5 \times 10^{-4}M$ ruthenium nitroso chloride solution in $0.1M$ hydrochloric acid, a 1-ml aliquot was diluted to 100 ml with $0.1M$ hydrochloric acid. Electrolysis of a 10-ml aliquot of the resulting $5 \times 10^{-6}M$ solution showed that 83 per cent of the ruthenium could be plated. After 38 days, another 1-ml aliquot of the same $5 \times 10^{-4}M$ solution was diluted to 100 ml with $0.1M$ hydrochloric acid and a 10-ml aliquot again electrolyzed. In this case, only 73 per cent of the ruthenium could be plated.

To determine accurately the rate at which the aging process occurred, 10-ml aliquots of a $5 \times 10^{-3}M$ ruthenium nitroso chloride solution in $0.1M$ hydrochloric acid were electrolyzed at various intervals during a two-month period. At the time the first aliquot was electrolyzed, the solution had aged one week. The results are plotted in Fig. 1 and show that the reaction which occurred obeyed a first order rate law. An aliquot of the same solution was electrolyzed one year after the solution had been prepared. In this case, only 2.5 per cent of the ruthenium could be deposited. It was interesting to note that, if the line drawn in Fig. 1 were extrapolated to one year, the amount that should have plated was 3 per cent.

Although only solutions containing $0.1M$ hydrochloric acid as the supporting electrolyte were carefully investigated with regard to the aging effect, the same general phenomenon was observed with $0.3M$ hydrochloric acid and with both 0.05 and $0.15M$ sulfuric acid. In all cases, it was possible to

restore the "unplatable" ruthenium to the freshly prepared condition by treatment with red fuming nitric acid. It appeared that either a slow hydrolysis or an irreversible complex formation may have been responsible for the observed effect.

Separation of "Platable" and "Unplatable" Ruthenium

The experiments previously reported strongly indicated that there were at least two different ruthenium species present in the very dilute solutions and perhaps even in the more concentrated solutions; one portion was readily reducible, and one was not. To confirm this point, two experiments involving the reduction of ruthenium nitroso chloride with mercury were carried out.

Previous attempts to obtain the electrodeposition of ruthenium nitroso chloride on a mercury cathode were unsuccessful because the mercury spontaneously

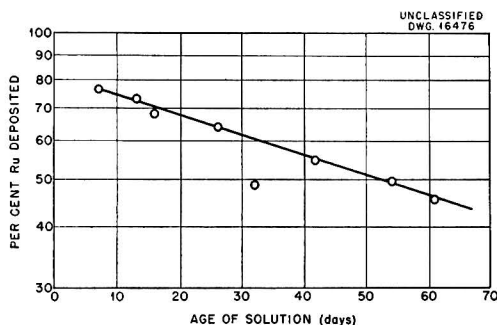


FIG. 1. The effect of age of the solution on the amount of ruthenium deposited from a $5 \times 10^{-3}M$ $RuNOCl_2$ solution.

reduced a part of the ruthenium. When a very dilute solution of ruthenium nitroso chloride was merely agitated with mercury, approximately 80 per cent of the ruthenium was removed from solution. Further contacting of the solution with new mercury did not remove additional ruthenium. (In perchloric acid solutions, mercury did not remove any ruthenium.) It thus appeared that mercury in a hydrochloric acid solution was capable of removing the same amount of ruthenium from dilute solutions as could be removed by electrodeposition at cathode potentials as high as -1.0 volt vs. S.C.E.

When a solution containing $5 \times 10^{-4}M$ ruthenium nitroso chloride in $0.1M$ hydrochloric acid (a solution from which complete deposition was possible) was shaken with mercury for a long period of time, 15 per cent of the ruthenium remained in solution. Further shaking did not remove additional ruthenium, and hence it appeared that the same situation, maybe to a different degree, existed in both solutions.

Influence of Cathode Metal

The cathode potential needed to obtain complete deposition of ruthenium from a $5 \times 10^{-4}M$ ruthenium nitroso compound has already been reported (1). Hence it was of interest to determine the deposition characteristics of the "platable" portion of the dilute solutions. Since it had been shown that the cathode metal greatly influenced the deposition potential of traces of silver (2), it was of interest to determine the deposition curve for traces of ruthenium on several different metals.

To determine what potentials were needed to deposit the "platable" portion of the ruthenium, 10-ml aliquots of a $5 \times 10^{-3}M$ ruthenium nitroso chloride

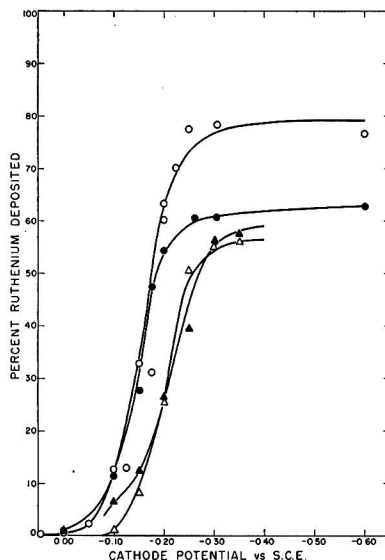


FIG. 2. Deposition curves on different metals for a $5 \times 10^{-3}M$ $RuNOCl_2$ solution in $0.1M$ HCl. \circ —platinum; \bullet —gold; \triangle —rhodium; \blacktriangle —palladium.

solution $0.1M$ in hydrochloric acid were electrolyzed at cathode potentials between 0.00 and -0.60 volt vs. S.C.E. using cathodes of the given metals. After a two-hour electrolysis, an aliquot of the solution as well as the cathode was counted.

Fig. 2 shows the deposition curves obtained using gold, platinum, rhodium, and palladium electrodes. The results obtained using tantalum electrodes are not shown because of the erratic behavior of the tantalum cathodes. No ruthenium was deposited on tantalum up to cathode potentials of -0.70 volt vs. S.C.E. At a cathode potential of -0.85 volt, 22 per cent was deposited; at -1.00 volt, 45 per cent; at -1.05 volts, 18 per cent; and at -1.10 volts, 25 per cent was plated.

The $E_{50\%}$ (the potential at which half of the

ruthenium was deposited) were -0.18 volt on platinum, -0.16 volt on gold, and -0.21 volt for both palladium and rhodium. Since the experimental error was considered to be about ± 30 mv and since the cathodes were not all cleaned in the same fashion, these figures do not necessarily indicate any real difference in the $E_{50\%}$ values. In this regard it was interesting to note that the $E_{50\%}$ reported for the deposition of ruthenium from a $5 \times 10^{-4}M$ ruthenium nitroso chloride solution in $0.3M$ hydrochloric acid was -0.22 volt (1). Hence it appears that the deposition potential may have been nearly independent of the ruthenium concentration and of the cathode material (except tantalum).

Fig. 2 indicated that different amounts of ruthenium were deposited on different metals. Since it has been pointed out that the ruthenium nitroso chloride solution changed with time, and since the deposition curves were not run at the same time, the per cents plated in Fig. 2 are not comparable. To determine the amount of ruthenium plated on dif-

TABLE II. Per cent ruthenium deposited on different cathodes from a $5 \times 10^{-3}M$ $RuNOCl_3$ Solution in $0.1M$ HCl at -0.55 volt vs. S.C.E.

Cathode metal	% Ruthenium deposited	Initial current (ma)
Platinum.....	64	200
Palladium.....	57	34
Rhodium.....	56	11
Gold.....	52	5
Copper.....	46	2

ferent metals, 10-ml aliquots of a $5 \times 10^{-3}M$ ruthenium nitroso chloride solution in $0.1M$ hydrochloric acid were electrolyzed using copper, gold, platinum, rhodium, and palladium cathodes. The electrolyses were carried out at the same time, and in each case a cathode potential of -0.55 volt vs. S.C.E. was used. The time of each electrolysis was two hours, and at the start the current passing through the cell was measured. The results are summarized in Table II. It should be noted that the higher the initial current, the greater the extent of deposition.

Since the above experiments suggested that the extent of ruthenium deposition was greater on metals of low hydrogen overvoltage, several electrolyses were performed using platinum black cathodes. The conditions of electrolysis were the same as those described above, except that a cathode potential of -0.40 volt vs. S.C.E. was used. In all cases, at least 95 per cent of the ruthenium was deposited and frequently as much as 98 per cent was deposited.

Since complete deposition was possible from a $5 \times 10^{-4}M$ ruthenium nitroso chloride solution, the

initial deposition of which produced a ruthenium cathode, it was thought that perhaps complete deposition of traces could be obtained on metallic ruthenium cathodes. Therefore, three depositions were carried out using copper cathodes which had been plated with inactive ruthenium. Preliminary experiments indicated that the exchange of ruthenium nitroso chloride solution with metallic ruthenium was either slow or nonexistent. The amounts of ruthenium plated in the three cases were 87 per cent, 77 per cent, and 84 per cent. Although the results were rather inconclusive, they definitely showed that complete plating did not occur on ruthenium cathodes.

Activation Energy for the Deposition Process

It was thought that a determination of the activation energy for the electrodeposition of ruthenium from a solution of the nitroso complex might give some indication of the rate-determining step and hence aid in elucidating the reaction mechanism. A $5 \times 10^{-3}M$ ruthenium nitroso chloride solution in $0.1M$ hydrochloric acid was chosen for this work. All electrolyses were carried out, using smooth platinum electrodes at a cathode potential of -0.60 volt vs. S.C.E. The specific reaction rates were obtained at four different temperatures.

In determining the value of the specific reaction rate, the counting rate for the solution after equilibrium was attained was subtracted in each case from the counting rates of all the other aliquots taken during the run. This was justified on the assumption that the activity left in solution at equilibrium was associated with a different ionic or molecular species which could not be electrodeposited at the potential used. When the rate curves using the corrected solution counting rates were plotted on semilog paper, straight lines were obtained, from the slopes of which the specific reaction rates were determined.

When the values for the specific reaction rates were plotted vs. the reciprocal of the absolute temperature on semilog paper, the graph shown in Fig. 3 was obtained. The slope of the upper part of the curve gives an activation energy of 6660 cal/mole while the slope of the lower portion gives an activation energy of 8020 cal/mole.

Deposition Studies with the "Unplatable" Ruthenium

The experiments described up to this point have shown that complete electrodeposition of traces of ruthenium could not be obtained at potentials which had given essentially complete deposition at higher concentrations. The following experiments describe the work that has been done in an effort to elucidate

the properties of the so-called "unplatable" fraction of the ruthenium.

In an acid solution it was difficult to increase the potential of a platinum cathode to high values because hydrogen evolution became excessive. The high hydrogen overvoltage of mercury made it possible to increase the potential of a mercury cathode to much higher values before hydrogen evolution became appreciable. Thus, an electrodeposition with a mercury cathode was carried out in order to determine whether or not the "unplatable" portion of

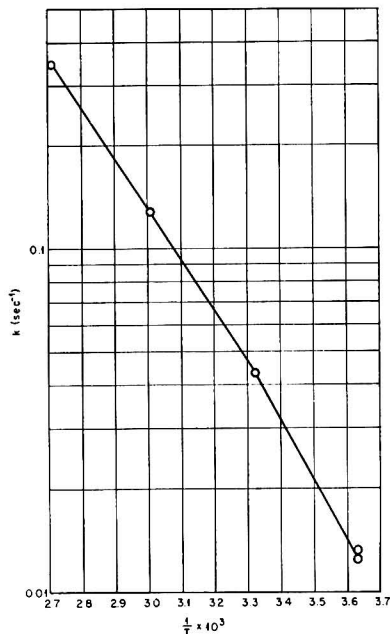


Fig. 3. Activation energy curve for the deposition of ruthenium from $5 \times 10^{-8}M$ $RuNOCl_2$ in $0.1M$ HCl.

the ruthenium could be deposited at relatively high negative potentials.

Two solutions were used for this study: a $5 \times 10^{-8}M$ ruthenium nitroso chloride solution in $0.1M$ hydrochloric acid, and a $1 \times 10^{-6}M$ ruthenium nitroso perchlorate solution in $0.1M$ perchloric acid, both of which had been previously electrolyzed with smooth platinum electrodes at -0.60 volt vs. S.C.E. One 10-ml aliquot of each of these solutions was placed in cells containing mercury cathodes. The cathode potential was maintained for one hour at a given potential and, at the end of this time, duplicate samples of the electrolyte were withdrawn and counted. Then the cathode potential was set at a more negative value, where the electrolysis was continued for another hour. This procedure was repeated until nearly all of the ruthenium was deposited. The deposition curves obtained are shown

in Fig. 4. Although the shapes of the two curves are somewhat different, the potentials at which 50 per cent of the ruthenium was deposited in each case were nearly the same.

At the completion of the electrolysis, the mercury was separated from the solution, and a count of the mercury indicated that essentially all of the ruthenium was present on the mercury surface. Samples of mercury from below the surface showed little or no activity, indicating an extremely low solubility of ruthenium in mercury.

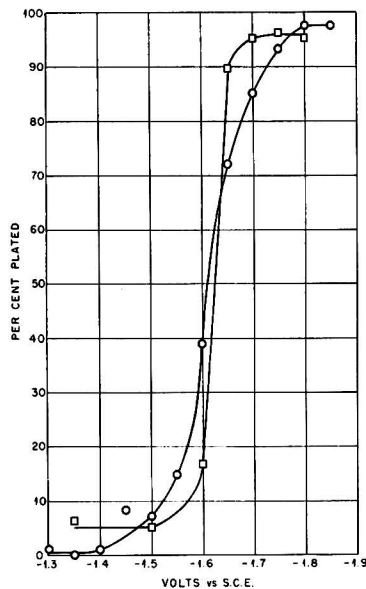


Fig. 4. Deposition curves for the "unplatable" ruthenium on mercury cathodes. \circ — $0.1M$ perchloric acid; \square — $0.1M$ hydrochloric acid.

Deposition onto Platinum Black Electrodes

Previous experiments had indicated that essentially complete deposition of ruthenium was possible from dilute ruthenium nitroso chloride in dilute hydrochloric acid when platinum black electrodes were used. It was not surprising to find that the same results were obtained when perchloric acid was used instead of hydrochloric acid.

Since the possibility existed that the ruthenium was not actually electrodeposited but rather adsorbed on the very large surface of the platinum black cathode, two electrolyses were performed to determine the amount of ruthenium that was apparently adsorbed and the amount that was actually electrodeposited. A 20-ml aliquot of $5 \times 10^{-8}M$ ruthenium nitroso perchlorate solution in $0.1M$ perchloric acid was electrolyzed at -0.60 volt vs. S.C.E., using a smooth platinum cathode. After the "plat-

able" ruthenium had been removed, 68 per cent of the ruthenium remained in solution. The solution was then divided into two equal portions and placed in each of two cells containing platinum black cathodes. The solution in one cell was merely stirred for three hours, while the other was electrolyzed at -0.40 volt vs. S.C.E. for the same length of time. At the completion of this time the cells were reversed, i.e., the cell that had been electrolyzed was disconnected and stirred, and the cell that had been stirred was connected and electrolyzed. During the stirring and electrolysis samples were taken. The results are shown in Fig. 5.

It should be mentioned that the potential of the platinum black with respect to the S.C.E. was -0.24 before stirring the solution, but rapidly changed to

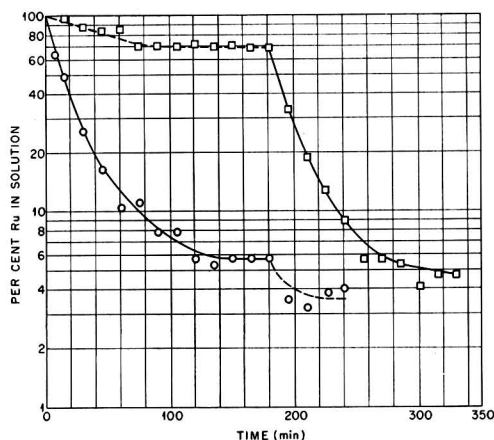


Fig. 5. The deposition and adsorption of the "unplatable" ruthenium on platinum black cathodes. \square —Stirred on platinum black for 3 hr, then electrolyzed; \circ —electrolyzed on platinum black for 3 hr and then stirred.

approximately $+0.70$ volt vs. S.C.E. as soon as stirring began. During the electrolysis the cathode potential was held constant at -0.40 volt.

While there was some ruthenium that appeared to be adsorbed on the platinum black, the largest portion of the ruthenium was actually deposited when the current was flowing. It was interesting to note that there appeared to be a certain amount of ruthenium removed from solution by adsorption even after the solution had been electrolyzed to a steady value.

DISCUSSION

On the basis of the experiments performed it appears certain that at least two different ionic or molecular species existed in dilute solutions of the ruthenium nitroso salts. Although nearly complete deposition was possible from solutions $5 \times 10^{-5}M$

(or greater) in ruthenium nitroso salts and only about 80 per cent from the more dilute solutions, reduction with mercury seemed to indicate that both solutions contained at least two very different entities and that they were nearly the same in the two solutions. It was also rather clearly shown that there appeared to be no equilibrium between the species (or else a very slow equilibrium).

When a dilute ($5 \times 10^{-6}M$ or less), freshly prepared ruthenium nitroso chloride solution was electrolyzed, the same amount of ruthenium could always be deposited under a given set of conditions. As these solutions aged, less ruthenium could be deposited from them. Hence the "platable" fraction of the freshly prepared solutions was gradually changed to an "unplatable" form. There appeared to be no difference between the original "unplatable" ruthenium and that which essentially grew from the "platable" form on standing. For example, both the original "unplatable" portion and that which was formed from the "platable" could be deposited on either platinum black electrodes or on mercury cathodes at high negative potentials.

The fact that ruthenium deposited at essentially the same cathode potential from concentrations ranging from 5×10^{-4} to $1 \times 10^{-8}M$ may not be surprising in view of the extremely irreversible nature of the deposition. However, it was interesting to note that either complete deposition from the more concentrated solutions or complete deposition of the "platable" fraction from the more dilute solutions was only possible when hydrogen was evolved from the cathode. In fact, the $E_{50\%}$ values are close to the potential needed for the discharge of hydrogen in the systems investigated. The fact that in dilute ruthenium solutions there was an apparent relation between the amount of ruthenium that could be deposited and the hydrogen overvoltage of the cathode metal also indicated that the discharge of hydrogen was of importance in the deposition of ruthenium.

The value of between 6660 and 8020 cal for the activation energy of the deposition of ruthenium from the nitroso complex was substantially higher than that usually associated with a diffusion-controlled process. For example the activation energy for the deposition of tungsten alloys has been reported as 2000 cal/mole, which is of the correct order for a diffusion-controlled process (7). It seems likely on the basis of magnitude of the activation energy that the rate-determining step in the deposition process may have involved a prototropic change. The values of the heats of activation for such processes are similar to those for the cathodic liberation of hydrogen, that is, 5000–10,000 cal/mole (8).

On the basis of the results discussed above, it is

proposed that in dilute solutions the "platable" fraction of the ruthenium is reduced by a mechanism involving either molecular or atomic hydrogen. It is possible that hydrogen reduces the nitroso group, thereby producing a ruthenium ion or molecule which is easily reduced. Hence, it is possible that the reduction of the ruthenium to the metal is brought about by electron transfer after the nitroso group has been destroyed or reduced. Since the "unplatable" fraction, which is not deposited under most conditions, can be deposited on platinum black at low potentials, it appears that the platinum black acts as a catalyst in the reduction of the "unplatable" fraction.

The fact that complete deposition of ruthenium is possible from solutions which contain enough ruthenium to form a number of atomic layers can be explained on the same basis. Since it has been shown that there are also at least two species in the more concentrated solutions, as in the dilute solutions, one must assume that the catalytic properties of

macro amounts of ruthenium during the deposition process are similar to those of platinum black.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Preparation of Yttrium and Some Heavy Rare Earth Metals¹

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ABSTRACT

A method was devised for preparing massive metallic yttrium, terbium, dysprosium, holmium, erbium, and thulium in high purity and high yields by reducing the rare earth chloride or fluoride with calcium metal in tantalum containers in an inert atmosphere. Ytterbium fluoride could be reduced only to the divalent state by the technique employed in this work. Estimated maximum melting points of some of these metals are given.

INTRODUCTION

In a program of study of metals in this laboratory, methods of preparing pure lanthanum, cerium, praseodymium, neodymium, and gadolinium in the massive metallic state have been devised (1, 2), which consisted of reducing the particular rare earth chloride with calcium in refractory oxide and tantalum crucibles. As quantities of the heavier rare earth salts have become available from other work in this laboratory (3), it was desired to prepare these metals also, and it was found that the methods which served so well for preparing the light rare earth metals could not be used unmodified for the heavy rare earths due to the higher melting points of the members of this latter group. In order to melt the product metal in the present work, it was necessary to heat the reaction mixture to temperatures at which rare earth chlorides were so volatile that poor yields were obtained, often with poorly formed products. However, when the less volatile rare earth fluorides were employed, excellent results were obtained.

In the past, yttrium has been prepared as a powdered metal by electrolytic and metallothermic methods (4-7). Thompson, Holton, and Kremers (7) obtained one sample of fused metal containing 1.9 per cent iron, but were unable to reproduce this work. The heavy rare earth metals were prepared by Klemm and Bommer (8) by heating the rare earth chlorides with potassium to give the rare earth metal powder mixed with the potassium chloride slag; the resulting mixture was used for x-ray studies. Yost, Russell, and Garner (9) in 1944 stated that "the yttrium (heavy rare earth) metals have not been isolated in any form remotely approaching the pure metal." Trombe (10) has more recently prepared dysprosium metal by the electrolysis of a fused-salt bath, collecting the dysprosium as a cad-

mium-dysprosium alloy in 60 per cent yields; a subsequent vacuum distillation was said to have removed the cadmium, leaving a dysprosium sponge.

PREPARATION OF RARE EARTH COMPOUNDS

The anhydrous rare earth chlorides were prepared by the method of Kleinheksel and Kremers (11) in which the rare earth oxide is dissolved in an excess of concentrated hydrochloric acid, and the resulting solution is evaporated to give the hydrated chlorides. These are then dried in a stream of dry hydrogen chloride gas at a pressure of about 4 cm Hg, with the temperature slowly raised to 400°C.

The anhydrous rare earth fluorides were prepared by dissolving the oxides in an excess of concentrated hydrochloric acid in a polyethylene beaker. An excess of 48 per cent hydrofluoric acid was added to precipitate the gelatinous hydrated rare earth trifluorides. Digestion on a water bath produced the granular anhydrous trifluoride from which the supernate was withdrawn; further heating on the water bath resulted in a free-flowing powder which was finally dried either by heating to 250°C in a vacuum, or by heating to 250°C in a stream of dry hydrogen chloride gas at a pressure of about 4 cm Hg. There is some evidence that a small amount of chloride (less than 1%) is present in the fluorides as a result of this latter treatment, but this does not interfere with the metallurgical processing.

REDUCTION TECHNIQUES

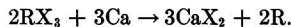
Calcium was the reductant used in all of this work, and was obtained as minus 10 mesh, plus 50 mesh material from another section of this laboratory, where vacuum distillation was employed to further purify a high purity calcium metal obtained from Dominion Magnesium Ltd.

The tantalum containers used in the reduction and melting operations were prepared from 0.0015 in.

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or 0.002 in. thick tantalum foil by a technique developed in this laboratory (12).

The reductions were carried out by mixing in an argon atmosphere the rare earth halide and 10 per cent more calcium than was required by the stoichiometry of the reaction:



The charge was placed in the tantalum container, capped with a perforated lid, and then transferred to an induction furnace consisting of a tantalum tube inductor surrounded by two concentric magnesium oxide radiation shields in a silica vacuum envelope. The furnace was evacuated and then filled to 1 atm pressure with argon. During the heating period, which usually lasted about 5 minutes, the reaction could be seen to take place when the charge suddenly became hotter than the furnace; this occurred between 600° and 800°C.

EXPERIMENTAL

Yttrium.—Since yttrium was much more available than the heavy rare earths, and since its metallurgy seemed likely to be similar to that of the heavy rare earths, it was first used as experimental material to determine the conditions which would most likely succeed with the heavy rare earths. Yttrium oxide 99.9 per cent pure, containing gadolinium oxide and dysprosium oxide as the major impurities, was the starting material.

In the first reduction of yttrium chloride, the charge was heated to about 1350° to 1400°C, when violent evolution of dense fumes began, and the furnace was shut off. The charge was found to have melted down well, but, on leaching, the yttrium metal was obtained as 14 grams of sponge, representing a 90 per cent yield; this material was arc-melted to give a solid button which contained 0.05 per cent calcium as the major impurity. Since yttrium chloride and calcium were the most volatile materials in the reaction mixture, the vaporized material could have been the result of a reversal of the reaction in which yttrium chloride and calcium were given off. To remove this possible source of trouble, yttrium fluoride was chosen as the next halide to reduce, as it reportedly has a much lower vapor pressure than the chloride (13). A 3.5-gram reduction of yttrium fluoride was carried out by heating the reaction mixture to a temperature of 1550°C and holding at this temperature for 5 minutes without evidence of the dense fumes observed when the chloride was reduced. The product was a fused disk of metal representing a yield of 99 per cent \pm ½ per cent. A second reduction of 35 grams of yttrium fluoride also gave a nicely formed disk, but the yield was only 84 per cent, due to a poor batch of fluoride. A subsequent

reduction on this same scale gave a 99 per cent \pm ½ per cent yield. All of these samples of yttrium contained about 0.1 per cent each of calcium and tantalum; the calcium content dropped to 200 ppm on vacuum melting in a tantalum crucible. The tantalum was found to be present as an intermetallic compound of undetermined composition which could be separated by dissolving away the yttrium in hydrochloric acid. In order to reduce this contamination, a reduction of yttrium fluoride was carried out in which the charge was heated as rapidly as possible to 1500°C, and then immediately cooled. By this technique, the tantalum content of the product metal could be reduced to less than 500 ppm at a sacrifice of about 5 per cent in the yield of metal.

To prepare yttrium metal powder in high yields, and still be able to use the more conveniently prepared yttrium fluoride, a reduction of yttrium fluoride was carried out in which sufficient calcium chloride was added to the charge so that the final slag composition was 20 per cent $CaCl_2$ -80 per cent CaF_2 , with a melting point of about 1140°C. By heating the reaction mixture to 1300°C, essentially complete reduction was obtained to give a sintered powder in a 98 per cent yield. However, even the $CaCl_2$ - CaF_2 mixture was difficult to remove completely from the powdered metal, and the chloride reduction remains the best method for preparing powdered metal. In the remelting of several samples of yttrium, the melting point as observed with an optical pyrometer was 1450° \pm 20°C.

Erbium.—Erbium oxide 99.9 per cent pure (0.1% other heavy rare earths) was the starting material for this work. As in the case of yttrium, erbium metal was prepared on a 35-gram scale by reducing the chloride and fluoride with calcium. Sponge metal was obtained when the chloride mixture was heated to 1400°C, and well-fused metal resulted when the fluoride mixture was heated to 1550°C. Very good yields (99% \pm ½%) were obtained when the reaction mixture was held for 5 minutes at 1550°C, with the introduction of about 0.1 per cent tantalum. By heating only to 1500°C and cooling immediately, as was done with yttrium, the tantalum content could be reduced to about 0.05 per cent at a sacrifice of about 5 per cent in the yield. Yost, Russell, and Garner (9) report a melting point for erbium of 1250°C, followed by a question mark. The authors' results would indicate a melting point between 1400° and 1500°C.

Holmium and dysprosium.—The holmium oxide used was 99 per cent pure, with 1 per cent dysprosium oxide and less than 100 ppm erbium oxide being the detectable impurities. The dysprosium oxide was 98 per cent pure, containing 2 per cent yttrium oxide. The fluorides of these elements were reduced

by the rapid heat technique to give 96 per cent yields on a 35-gram scale. The melting points of these metals, as observed in remelting operations by an optical pyrometer, were in the range 1400°–1525°C.

Terbium.—A 10-gram sample of 60 per cent Tb_4O_7 (balance, mixed heavy rare earths) was converted to the fluoride and then reduced by the rapid heat technique at a temperature of 1550°C. A fused sample of metal was obtained which represented a yield of about 80 per cent. The lower yield on this smaller scale of reduction could undoubtedly be improved by more rigorous degassing of the furnace and by maintaining a more anhydrous atmosphere around the charge during handling. Since the metal obtained was not pure terbium, the fact that it melted below 1550°C cannot be used as a basis for stating that the melting point of the pure element is also below this figure.

Thulium.—Ten grams of thulium oxide, containing 2 per cent ytterbium oxide as the only detectable impurity, was the starting material for the thulium preparation. This case was particularly interesting since ytterbium was known to have a stable divalent state like samarium, and would probably behave like samarium. In the reduction of gadolinium-samarium mixtures, it was found (2) that the samarium remained in the slag, effecting a very clean separation from gadolinium in the preparation of the metal. The thulium fluoride-calcium mixture was heated by the rapid heat technique to about 1600°C, producing a 70 per cent yield of fused ytterbium-free thulium metal. The melting point of thulium is estimated to be between 1500° and 1600°C. The lower yield obtained in this reduction could undoubtedly be improved by the modifications recommended for terbium. An analysis of the slag showed the ytterbium to be present in this phase.

Ytterbium.—Although the thulium reduction had given a clear indication that ytterbium fluoride could not be reduced to the metallic state by calcium, an attempted reduction was carried out on a 3.5-gram scale. When the temperature of the reaction crucible reached 1050°C, fumes began distilling from the reaction mixture, and, as the heating continued, the fumes finally became so dense as to obscure all light from the reaction vessel. From the length of the

heating period, it was estimated that the temperature reached at least 1550°C. On opening, a small bit of fused salt was found in the crucible which x-ray diffraction analysis showed to be calcium fluoride slightly contaminated by another phase. Inside the furnace chamber, a dark green, sooty deposit was found, which, because of its color, was assumed to be ytterbous fluoride. This would indicate a higher volatility for this compound than is consistent with data in literature (13).

X-ray diffraction patterns were obtained of powdered specimens of all of these metals, and, in general, they agreed within the limits of experimental error with the data given by Klemm and Bommer (8).

Due to their unavailability in the past, the heavy rare earth metals have not received extensive study. Further work is now under way in this laboratory on these metals; results will be published in the future.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Polarography in Glycerol at Elevated Temperatures¹

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ABSTRACT

The advantages of polarography at higher temperatures are that degassing is not necessary, maxima are less frequent, and sensitivity is greatly increased. The variation of diffusion current was linear with molarity and with temperature. The half-wave potentials tended to shift to more negative values with increasing temperature and concentration. The diffusion current varied inversely as the square root of the viscosity of the solvent. Benzaldehyde, fumaric acid, meta- and para-nitrobenzoic acid, and nitro-cycloheptane were reduced at the dropping mercury electrode. The supporting electrolyte was 0.1M lithium chloride, with silver-silver chloride as a reference electrode. The temperature range was 70° to 120° C.

INTRODUCTION

Up to the present, few papers have been published on polarographic reductions in nonaqueous solvents. Even fewer publications have appeared in which a viscous solvent such as glycerol has been used. Most such work has been done in aqueous or semi-aqueous solvents at room temperature, and, as a result, few data have been collected on the effect of temperature at the dropping mercury electrode.

Nejedly (1) made polarographic analyses in aqueous solution at temperatures up to 100°C. The diffusion currents, in general, increased with temperature about 2.5 per cent per degree. The temperature coefficient of the diffusion current was deduced theoretically by Ilkovic (2). For the majority of metallic ions, the increase in diffusion current should be near 1.63 per cent.

Skobets, Turov, and Ryabokon (3) demonstrated that at 50°–60°C the waves obtained at stationary electrodes are higher than at normal operating temperatures, and that no maxima were observed.

Radin and De Vries (4) used anhydrous glycerol as solvent at room temperature and obtained waves for 1-nitropropane and 2-nitropropane. Waves were not obtained for larger molecules since they could not diffuse in the viscous solvent.

In this research, polarographic reductions were investigated at elevated temperatures to ascertain if such reductions were feasible in glycerol as solvent, and if the Ilkovic equation was obeyed for the organic compounds studied.

EXPERIMENTAL PROCEDURE

The current-voltage curves were obtained with a Sargent Model XXI recording polarograph. The gal-

vanometer was undamped to avoid the necessity of a correction in the calculation of the half-wave potentials. Prior to use, the instrument was checked with a standard resistor.

An oil-filled thermostat was used in this investigation and controlled to $\pm 0.2^\circ\text{C}$.

A silver-silver chloride electrode served as the reference electrode, and was prepared from 2 in. of No. 22 platinum wire, wound into a tight spiral and sealed in a short length of 8-mm Pyrex tubing. Silver was electroplated on the wire by electrolyzing for 3 hr in a 0.05 molar $\text{KAg}(\text{CN})_2$ solution at 4 ma. The electrode was then used as the anode for one-half hour in 0.1N HCl solution.

The same capillary, made from marine barometer tubing, was used for all the determinations reported in this paper. The value of $m^{2/3}t^{1/6}$ was in the range 2.44 to 2.53 for all the temperatures used.

Materials

The organic compounds, benzaldehyde, fumaric acid, *m*-nitrobenzoic acid, *p*-nitrobenzoic acid, and nitrocycloheptane, were carefully purified in the appropriate manner either by fractional distillation or recrystallization from solvents.

Lithium chloride was synthesized from reagent grade HCl and Li_2CO_3 , and was recrystallized from methyl alcohol to purify it.

The glycerol used was distilled and the fraction which came over at 145°–150°C at 3 mm Hg was collected.

It was easiest to make up the solutions by weighing the constituents. In practice a stock solution, which was 0.1M with respect to LiCl, was prepared, and sufficient amount of the reducible compound was added to give a solution of approximately five times the desired concentration. This solution was then diluted with glycerol, 0.1M in LiCl, to the desired concentration. It was found that the major-

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ity of the compounds dissolved more readily if the glycerol was preheated to 100°C.

Due to the hygroscopic nature of the glycerol, the polarographic cell was kept at 100°C for 20 min before any determinations were made at a lower temperature. This was deemed sufficient to remove any residual traces of water. Degassing of the solutions was not necessary for any of the analyses.

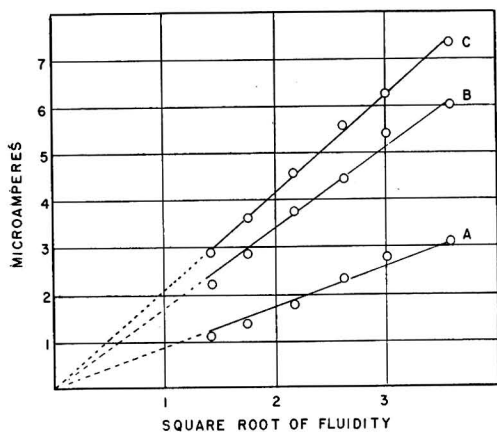


FIG. 1. Variation of diffusion current of *m*-nitrobenzoic acid with viscosity. A—0.00033 molar; B—0.00070 molar; C—0.00090 molar.

TABLE I. Variation of diffusion current with temperature (0.00033M *m*-nitrobenzoic acid)

Temp, °C	Diffusion current, μa , i_d	$m^{2/3}t^{1/6}$	Viscosity, poises, η	Product, $i_d\eta^{1/2}$
70	1.11	2.49	0.506	0.79
80	1.35	2.50	0.322	0.77
90	1.76	2.51	0.212	0.81
100	2.30	2.52	0.146	0.88
110	2.76	2.52	0.105	0.85
120	3.03	2.52	0.078	0.85
130	3.39	2.53	0.060	0.83

Temperatures higher than 140°C were not used since the silver-silver chloride electrode began to behave erratically. In many cases the plateaus of the curves became extremely irregular above 130°C.

When the recording polarograph indicated that the reduction potential was reached, a mercury drop collector was placed underneath the capillary, and 25 drops were timed and collected. This gave the data for the calculation of $m^{2/3}t^{1/6}$ for each run. After each determination, a Serfass conductance bridge was used to measure the cell resistance. This was used in correcting the half-wave potential for the *IR* drop through the cell.

RESULTS AND DISCUSSION

Benzaldehyde was the first compound reduced in this investigation. A 0.0012 molar solution in 0.1N

LiCl was prepared and polarographic determinations run from 110° to 140°C at 10° intervals. At 110° and 120°C, well-defined waves were obtained, but

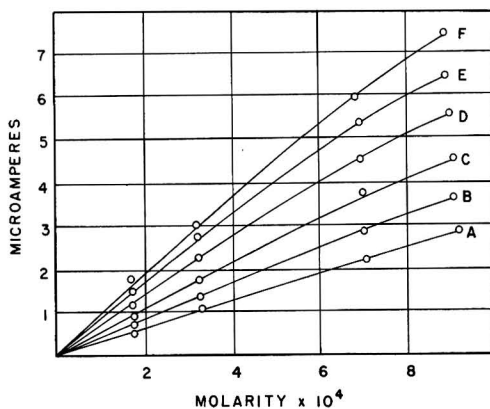


FIG. 2. Variation of diffusion current of *m*-nitrobenzoic acid with concentration and with temperature. A—70°C; B—80°C; C—90°C; D—100°C; E—110°C; F—120°C.

TABLE II. Data for 0.00018M *m*-nitrobenzoic acid

Temp, °C	Time for 25 drops, sec	Weight for 25 drops, mg	$m^{2/3}t^{1/6}$	Diffusion current, i_d , μa	Half-wave potentials
70	78.8	230	2.47	0.59	-0.80
80	77.6	227	2.47	0.74	-0.81
90	77.2	228	2.48	0.93	-0.81
100	76.4	226	2.49	1.22	-0.82
110	75.9	225	2.48	1.59	-0.82
120	75.5	226	2.50	1.77	-0.84
130	74.6	224	2.49	2.10	-0.82
140	73.2	223	2.48	2.18	-0.82

TABLE III. Dependence of diffusion current on concentration (*m*-nitrobenzoic acid)

Molar conc	Diffusion current, 70°C	Half-wave potential, 70°C	Diffusion current, 80°C	Half-wave potential, 80°C
0.00018	0.59	-0.80	0.74	-0.81
0.00033	1.11	-0.80	1.35	-0.81
0.00070	2.23	-0.80	2.85	-0.81
0.00090	2.87	-0.82	3.60	-0.82
0.00127	3.96	-0.82	4.98	-0.82

those at 130° and 140°C were considerably reduced in step height, indicating that the benzaldehyde was distilling out of the glycerol. These results indicate the limitations imposed on reductions at higher temperatures. The compounds selected must have high enough boiling points to prevent their distillation from the cell solution. At 110°C, the diffusion current was 3.54 μa , the drop time of the capillary was 2.9 sec, and the value of $m^{2/3}t^{1/6}$ was 2.49. The half-wave potential was -1.41 volts measured with the silver-silver chloride reference electrode. This makes the $E_{1/2}$ -1.36 volts on the saturated calomel elec-

trode scale, assuming that the activity of the Cl^- of the 0.1*N* LiCl in glycerol is about 0.08.

The reduction of fumaric acid was studied at 10° intervals in the range from 100° to 140°C, using a 0.000985 molar solution, with 0.1*N* LiCl as supporting electrolyte. A single wave was obtained in each case, the step height increasing with temperature, as one would expect. At 100°C, the diffusion current was 2.21 μa and the value of $m^{2/3}t^{1/6}$ was 2.43. The half-wave potential was -1.20 volts, measured against the Ag-AgCl electrode.

The reduction of *p*-nitrobenzoic acid was studied at 10° intervals from 70° to 120°C, using a 0.00094 molar solution in 0.1*N* LiCl. A single wave, with an almost vertical step and well-defined plateau, was observed in each case. At 100°C, the diffusion current was 5.72 μa , the value of $m^{2/3}t^{1/6}$ was 2.51, and the half-wave potential was -0.80 volt.

Extensive determinations were made of *m*-nitrobenzoic acid at varying concentrations and different temperatures. Four solutions, ranging from 0.00018 to 0.00090 molar, were used at temperatures from 70° to 130°C. In order to investigate the stability of the solutions, a cell would be heated to 100°C for several hours and a second curve obtained. The values for the diffusion current did not vary more than 0.04 μa in any of the curves obtained.

The waves were regular and well-defined for temperatures from 70° to 120°C. In many of the waves, particularly those above 110°C, a slight dip occurred before the wave levelled off to its constant value. This irregularity was not always apparent and did not hinder the measurement of the diffusion current and half-wave potentials. It was eliminated by the addition of small amounts of maxima suppressor or trace amounts of water. Moreover, it was not a function of the reducible species, as it occurred in most of the compounds investigated. It was, therefore, attributed to some solvent effect. At temperatures above 120°C, the plateaus became irregular and difficult to measure. An attempt was made, without success, to eliminate this irregularity by using a mercury pool in place of the Ag-AgCl reference electrode. Small concentrations of maxima suppressor also had no effect. At still higher temperatures, up to 160°C, decomposition of the reference

electrode occurred, and the diffusion current no longer varied in a linear manner with temperature.

From 70° to 130°C, the diffusion current increased linearly by a threefold factor. This increase is associated with the decrease in viscosity of the solvent, and is approximately proportional to the square root of the fluidity. Fig. 1 illustrates the linear relationship between the diffusion current and the square root of the fluidity for three solutions of *m*-nitrobenzoic acid, with 0.1*N* LiCl as supporting electrolyte. The data for the 0.00033 molar solution is given in Table I. The data in the last column show to what extent this linear relationship is true. The viscosities of glycerol were obtained from the literature (5, 6).

The diffusion currents were proportional to the molarity of the compound, as required by the Ilkovic equation. A slight tendency to deviate from linearity can be noticed in the curves for the data obtained at 90°C and higher (see Fig. 2). At 70° and 80°C, the linear relation held very well. Typical data for 0.00018 molar *m*-nitrobenzoic acid solutions at various temperatures are given in Table II, and data for various concentrations at 70° and 80°C in Table III.

The last compound investigated was nitrocycloheptane, which had not previously been reduced at the dropping mercury electrode. It exhibited a single, well-defined wave with a half-wave potential of -1.04 volts at 80°-100°C. A 0.0001 molar solution in 0.1*N* LiCl as supporting electrolyte showed a diffusion current of 3.84 μa and the value of $m^{2/3}t^{1/6}$ was 2.51 at 80°C.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Determination of Current Efficiency of Diaphragm Alkali-Chlorine Cells by Gas Analysis¹

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ABSTRACT

A description is given of a method for determining current efficiency of an alkali-chlorine plant simply by an analysis of a cumulative sample of chlorine cell gas, rather than by the more laborious method of measurement of the entire production and current input. A method of obtaining a 24-hr cumulative sample of gas at a uniform rate is described. Essentially the method of calculation is based upon the fact that the ratio of carbon dioxide and oxygen to chlorine in the cell gas depends upon the current efficiency of cell operation.

INTRODUCTION

Murray and Kircher (1) described a method for determining the current efficiency of the Hooker Type S diaphragm cell for the electrolysis of sodium chloride brine by means of the analysis of the chlorine gas. The method was worked out during an investigation of the effect of various operating conditions on the current efficiency of a cell. Conditions such as brine feed rate, brine purity, current density, etc., were controlled rather accurately on one cell, and all significant analytical data were taken by the methods of Kimball and Tufts (2). The present paper describes how the gas analysis method has been applied in determining current efficiency for an entire plant. During the past five years, the method has been used for daily determination of current efficiency.

PRINCIPLE

The method is based on Faraday's law as applied to the reactions taking place in the anode compartment of the cell (1). The anode processes are the discharge of chloride ions to form chlorine gas and the discharge of hydroxyl ion or other oxygen-bearing ions to form oxygen. Any process causing oxygen formation requires expenditure of four Faradays per mole, whereas the formation of chlorine requires two Faradays per mole. A considerable portion of the anodically formed oxygen combines with the graphite anode to form carbon dioxide and carbon monoxide. Hence, in calculating current efficiency from gas analysis, oxygen present in the form of carbon monoxide and carbon dioxide must be accounted for, as well as free oxygen.

Chlorine formed at the anode which dissolves in

the anolyte and enters into reactions such as the formation of chlorate ion is not accountable by gas analysis, but may be estimated separately from analysis of the anolyte.

Chlorine current efficiency may be expressed as

Chlorine CE

$$= \frac{\%Cl_2}{\%Cl_2 + \%CO + 2(\text{net } \%CO_2 + \text{net } \%O_2) + Cl_2 \text{ (dissolved)}} \quad (1)$$

The compositions are all in volume per cent. Net CO_2 is that formed at the anode which equals total carbon dioxide in the chlorine gas, minus carbon dioxide in the chlorine gas derived from carbonate in the feed brine.

Net O_2 is that formed at the anode, which equals oxygen in the chlorine gas, minus oxygen derived from leakage of air into the chlorine gas.

Dissolved chlorine is given by the loss of chlorine from the anode gas by solution in the anolyte in the form of Cl_2 , $HOCl$, ClO^- , and ClO_3^- , and passage through the diaphragm, expressed as volume per cent chlorine in the chlorine gas.

The magnitude of the various anode processes is shown in Fig. 8 of Reference (1).

The analytical data for determining the quantities for the above equation are outlined briefly as follows. Chlorine gas is collected continuously at a uniform rate for a period, such as 24 hours. A portion of the accumulated sample is withdrawn into a sampling device containing an alkaline arsenite solution free of chloride and carbonate. Oxygen, hydrogen, carbon monoxide, and nitrogen are determined by an Orsat analysis of the gas not absorbed by the arsenite solution. Chlorine is determined by a chloride determination of the arsenite solution, and carbon dioxide is determined by an evolution method from another aliquot of the arsenite solution.

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The carbon dioxide derived from the brine is based upon the analysis of a brine sample collected during the same period as the gas sample, and upon the ratio of NaCl to NaOH in the caustic liquor (which indicates accurately the amount of brine fed to the cells corresponding to a given chlorine production).²

The oxygen content in the chlorine derived from leakage of air into the chlorine can readily be determined from the value for nitrogen obtained in the Orsat analysis of the gases.

The "free chlorine" and chlorate content of the anolyte, multiplied by the volume of flow through the diaphragm, was determined for several cells operating under typical conditions. A factor of 0.6 per cent was obtained as a typical value for our conditions, and was assumed as a constant in the formula. This factor, of course, is not a constant and, hence, for any determinations where the current efficiency is considerably lower than the typical 95-97 per cent, experimental values for "dissolved chlorine" in the anolyte should be obtained.

The current efficiency obtained by (I) is the chlorine current efficiency. In the case where the brine feed is neutral and the sulfate content is relatively low, the chlorine current efficiency is equal to the caustic current efficiency.

Alkali in the brine results in the chlorine efficiency being lower than the caustic efficiency in an amount equivalent to the alkali added. Conversely, acid in the brine results in the chlorine current efficiency being higher than the caustic current efficiency. Reducing substances such as sodium tetrathionate (3), which may be added to the brine for the purpose of reducing graphite anode consumption and chlorate content of the caustic soda, react with chlorine in the anolyte to produce acid. The effect on the gas analysis is the same as adding acid in the brine; however, since chlorine is consumed, the chlorine current efficiency indicated by the formula would not be a true measure. A true measure may be obtained by subtracting, from the current efficiency indicated, the current efficiency equivalent to the reducing agent added. Actually, however, when acid brine or reducing agents in brine are used, the oxy-

gen and carbon dioxide content of the chlorine tends to become so small in relation to the correction factors that gas analyses are more profitably used as a guide than as a measure.

The sulfate content of the brine does not enter into the calculations of current efficiency, since sulfate discharge at the anode has the same effect as hydroxyl ion discharge in that it results in the formation of oxygen and carbon dioxide (1). Hydrogen ions produced by sulfate discharge neutralize hydroxyl ions coming through the diaphragm; hence, when the sulfate discharge is appreciably less than the hydroxyl ion migration through the diaphragm, neither the chlorine current efficiency nor caustic current efficiency are affected by the presence of sulfate. Normally, with 5 g/l Na₂SO₄ or less in the brine, sulfate discharge amounts to less than 1 per cent current efficiency, whereas hydroxyl migration through the diaphragm may typically amount to 4 per cent.

METHOD OF OBTAINING CONTINUOUS SAMPLE

In order to calculate a daily current efficiency, it is necessary to obtain a sample of chlorine gas which represents the average production for a day. The most convenient point from which to take the gas sample for analysis is from the line following the gas compressors. At this point, the gas has been cooled and dried and is typically under a pressure of approximately 30 psig. Sampling has been carried out by two different methods. The first method used was to displace sulfuric acid continually from a 19-liter glass carboy, the displaced acid flowing into a second glass carboy, having a 47-liter capacity. The second carboy was elevated above the first so that the gas sample was always under pressure. A needle valve in the line to the first bottle was regulated so that the flow of gas could be adjusted to uniform rate to displace approximately 15 liters of acid over a 24-hr period. The first bottle was painted to prevent action of light on the gas mixture; a safety seal was provided to prevent excessive pressure being applied on the glass bottles, and a bubbling bottle was inserted in the feed line after the needle valve to provide a visual guide for adjustment of the needle valve.

Although the head of sulfuric acid against which the gas was admitted to the sampling bottle increased by approximately 18 in. from beginning to end of the sample period, the pressure drop across the needle valve varied only approximately 4 per cent because of the 30 psig pressure at the valve inlet. This sampler, although extremely simple and satisfactory with respect to its intended function, was considered hazardous because of the possibility of breakage of the glass and spillage of sulfuric acid.

² For simplicity, it has been assumed that all sodium carbonate introduced in the brine is released as CO₂ in the chlorine; however, samples of cell liquor carefully withdrawn in a CO₂-free atmosphere have shown a carbonate content corresponding to approximately 1/10 of the carbonate in the brine (1). Hence, it would be more accurate to multiply the amount of CO₂ introduced in the brine by a factor of 0.9 or other experimentally determined factor which might be obtained with a given type of cell, given temperature, pH of anolyte, etc. If this factor were included, it would presumably be determined as an average of several determinations, and would be included as a constant, rather than a variable, in the equation.

Hence, it has been replaced by a second type of sampler.

The second type of sampler, shown in Fig. 1, consists of a pair of 150-lb chlorine cylinders which can be used alternatively as receivers. Each cylinder is evacuated before use by a mechanical vacuum pump to 0.2–0.3 in. mercury, and then filled over a period

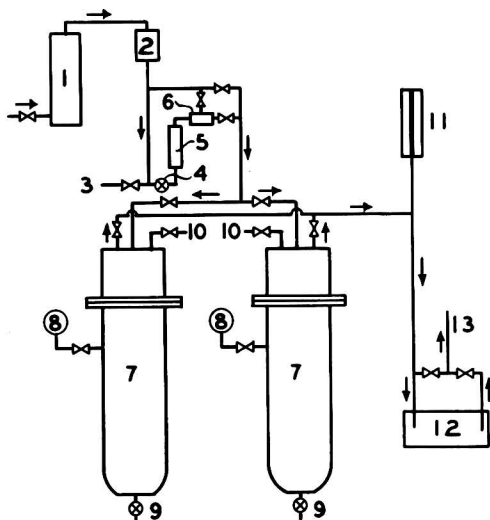


FIG. 1. The cumulative chlorine gas sampler is made up of the following parts: x—Lunkenheimer steel, bar stock, needle valves, $\frac{1}{4}$ in.; 1—Aluminum gel drier, glass wool packed at ends, length 19 in., (480 mm) diameter 3 in. (77 mm), made from 3-in. pipe; 2—activated carbon cartridge, 2 in. (51 mm) in diameter and 7 in. (179 mm) long; 3—snatch sample line; 4—Hoke valve, bellow seal, $\frac{1}{4}$ in., Catalog No. 433; 5—flowmeter, Fischer-Porter Rotameter to pass 130 cc/min of Cl_2 at 35 psig, stainless steel fittings and glass float; 6—flow controller, Moore flow controller, Model 63 SU, connections $\frac{1}{4}$ in. IPS, manufactured by Moore Products Company, Philadelphia, Pa.; 7—sample cylinders, inverted 150 lb (68 kg) chlorine cylinders cut, flanged, and joined by the flanges; 8—gauges, Crosley pressure-vacuum chlorine gauges, 30 in. (760 mm) vacuum to 30 psig (2.1 kg/cm²); 9—plugcocks, $\frac{3}{8}$ in. Merco Nordstrom; 10—cumulative sample lines; 11—mercury manometer, protected by a Fluorolube seal, Merriam Instrument Company, Type W, Model A-786, Ser. No. C-11373, range 12 in. (307 mm), Fluorolube from the Hooker Electrochemical Company; 12—Cenco pressovac 4 pump, filled with Fluorolube S; 13—ventline to low pressure turbine.

of 24–72 hours. Dry, compressed gas at approximately 30 psig is fed through an alumina gel filter, 1, an activated carbon filter, 2, manual control valve, 4, rotameter, 5, and “flow controller,” 6, to either of the evacuated cylinders, 7. The activated alumina and activated carbon filters remove traces of organic material, pipe scale, etc., which might cause blockage of the valves or flow controller. The filters are renewed after approximately three months

of operation. Manual control valve 4 is set to give a flow rate such that the cylinder is filled to 20–25 psig pressure within the sampling period desired. A flow rate of 100 ml/min is required for a 24-hr sample. The flow controller maintains a constant pressure on the downstream side of valve 4 so that there is a constant differential pressure across valve 4 at any given setting of that valve.

When the sample has been collected, the cylinder is closed off from the feed line; the alternate cylinder, having been previously vented and evacuated, is connected to the feed line, and the flow of chlorine gas is regulated by valve 4 again to fill the cylinder in the period desired. This period is usually 24 hours, but may be extended over a weekend.

The method of analysis used for the chlorine gas sample is that developed by Kimball and Tufts (2) for earlier work on the current efficiency method. This consists of absorbing a chlorine gas sample in alkaline arsenite contained in a specially constructed, jacketed, absorbing pipette. The residual gases over the alkaline solution are transferred to an Orsat apparatus, measured, and analyzed by conventional methods. The absorbing solution is rinsed into a volumetric flask and made up to volume with CO_2 -free water. An aliquot is titrated by the Volhard method as modified by Caldwell and Moyer (4) for chlorine, and another aliquot is analyzed for CO_2 by an evolution method, followed by absorption in excess alkali, and titration of the excess alkali with acid.

Omission of the cooling reservoir around the absorbing pipette still permits absorption of 5–7 liters of gas satisfactorily without getting too warm, and is much simpler to build and use.

Improvements in the analysis of the residual gases increased the efficiency and speed with which these analyses are carried out.

It was found desirable to remove the traces of less volatile constituents, chlorocarbons and chlorohydrocarbons, from the residual gases before their analysis in order to prevent fouling of the combustions. This was done by installing a cold trap pipette on the gas analyzer and passing the gas through it until no further contraction is observed. Dry ice and methanol were added as coolant.

The gas so treated can be passed over the platinum spiral to burn the hydrogen to water and the carbon monoxide to carbon dioxide. The carbon dioxide formed is absorbed in 30 per cent NaOH solution, and is a measure of the carbon monoxide. The hydrogen is calculated from the contraction. The residual oxygen is absorbed in a copper- NH_4OH pipette. Total oxygen is calculated from the residual and that used in burning hydrogen and carbon monoxide.

CALCULATION OF CURRENT EFFICIENCY

The volumes of all the gases are corrected to standard conditions, and the volume per cent of each is calculated. The cell liquor, for the period over which gas is collected, is analyzed for salt and caustic soda. The feed brine is analyzed for salt and carbon dioxide (carbonate).

TYPICAL CALCULATION OF CHLORINE CURRENT EFFICIENCY

Analytical data and constants:

Salt caustic ratio of the cell liquor (g NaCl/1000 g NaOH).....	1189
Salt required to produce 1000 g NaOH (theory).....	1461 g
Chlorine equivalent to 1000 g NaOH.....	886.3 g
Weight of chlorine gas per liter STP.....	3.214 g
Weight of carbon dioxide per liter STP.....	1.977 g
NaCl in feed brine.....	26.55%
Equivalent CO ₂ in feed brine.....	0.031%
Chlorine gas analysis (volume per cent).....	
Chlorine.....	96.66%
Oxygen.....	0.94%
Carbon dioxide.....	1.77%
Carbon monoxide.....	0.08%
Nitrogen.....	0.40%
Hydrogen.....	0.14%
Condensables at -78°C.....	0.01%

Calculation:

$$\frac{(1189 + 1461)(0.3214) (0.967)}{886.3} = 0.929 \text{ g wt of NaCl required to produce the chlorine in 100 ml of gas sample}$$

$$\frac{0.929 (0.00031)}{0.2655 (0.001977)} = 0.55 \text{ ml CO}_2 \text{ from the brine}$$

$$= 0.55 \text{ volume \% CO}_2 \text{ from the brine in the gas sample}$$

$$1.77 - 0.55 = 1.22\% \text{ CO}_2 \text{ from the oxidation of graphite anodes}$$

$$\frac{0.40 (0.2049)}{0.79} = 0.10\% \text{ O}_2 \text{ from air}$$

$$0.94 - 0.10 = 0.84\% \text{ O}_2 \text{ from the cell reaction}$$

Chlorine current efficiency =

$$\frac{96.66(100)}{96.66 + 0.08 + 2(1.22 + 0.84) + 0.6} = 95.3\%$$

Chlorine current efficiency figures determined in this way and tabulated or graphed together with other operating data are a valuable control on cell operation. Also, in conjunction with ampere-hour meter readings on the direct current to the cells, the current efficiencies are used to determine cell production figures.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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The Electrochemistry of the First Layers of Electrodeposited Metals¹

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ABSTRACT

The electrolytic deposition of the first few atomic layers of a number of metals on gold and silver has been studied by the method of charging curves. Preliminary results have indicated the value of the method for studying the first stages of electrodeposition; in particular, the variations in the nature of the binding of the first atomic layers to the underlying metal have been found.

INTRODUCTION

Very little is known of the early stages of the processes which occur when a metal is deposited by electrolysis from aqueous solutions. It may be expected that the early stages are of importance in determining the physical properties of the final deposit. Most of the work in this field has been concerned either with the deposition of radioactive substances from dilute solutions (1), or has been incidental to other work.

Oberbeck (2) and, more recently, Nichols (3) showed that an electrodeposit of copper on platinum of the order of a few atoms thick behaved as a copper electrode. Bowden (4) followed the deposition of traces of metal impurities on a mercury cathode by observing the rate of depolarization of the cathode on open circuit. In the most recent investigations with radioactive metals, Rogers (5) studied the deposition of traces of radioactive silver on a platinum electrode. He showed that a film of the order of the first monolayer deposits at a more noble potential than the reversible potential calculated from the Nernst equation. Rogers interpreted this by developing the concept of Herzfeld (6), who stated that the activity of a deposit should vary with the fraction of the surface covered. Rogers also added an additional term to the Nernst equation to take into account the energy of alloy formation of the deposit with the electrode.

Bowden and Rideal (7) devised an experimental method for studying the variation of potential with the quantity of electricity passed in the earliest stage of the polarization of an electrode. The method has been used extensively to study the process occurring before the cathodic evolution of hydrogen and the anodic evolution of oxygen. Whenever there is a rapid linear variation of potential with the quantity

of electricity passed, the process is generally identified as the charging of the electric double layer of the metal-solution interface, and, from the slope of the graph, the capacity can be obtained since $C = q/v$, where C is the capacity in microfarads, q the quantity of electricity in microcoulombs, and v is the change of electrode potential in volts corresponding to q .

When discharge of ions occurs to give adsorbed products or compounds with the electrode material, there is a step in the charging curve. This step indicates (a) the potential range over which the adsorption or reaction occurs, and (b) the quantity of electricity involved in the adsorption or reaction. Hence, the number of atoms participating in the process can be found, and, if the number of metal atoms per unit area of the electrode surface were known, the nature and thickness of the film formed could be worked out precisely. The main difficulty in interpreting charging curve data is the determination of the number of metals atoms per unit area of electrode surface; this involves a knowledge of the ratio of the real to the apparent area of the electrode surface, about which there is considerable uncertainty. A measure of this ratio can be obtained by Bowden's and Rideal's (7) method, in which the capacity of the double-layer region on the "charging curve" of the electrode is compared with that of mercury, for which the ratio is taken to be unity. This method at least enables the order of the film thickness to be determined. Wagner (8) has recently used the method of comparing polarization capacities for determining the relative areas of silver surfaces prepared in different ways.

The method of charging curves was originally developed by Bowden and Rideal (7) for the study of the electrodeposition of thin metallic films. They and subsequent workers (9) became interested in the study of adsorbed oxygen and hydrogen films, and to date little work has been done on metallic deposits.

In the present investigation, the method of

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charging curves was developed primarily to study oxide films on gold and silver, and the effect of anions on these films. However, during the course of the work, some metallic films were studied, and this paper will provide a brief account of an exploratory research concerned with the initial stages of the deposition of metal films on gold and silver.

EXPERIMENTAL

Charging curves may be obtained by either of two methods, one suitable for high current densities, the other for low current densities. In work at high current densities, the electrode is polarized at a constant current density, and the very rapid variation of the potential is followed oscillographically (10). At very low current densities, the change in potential occurs slowly, and is followed over a period of minutes by taking successive readings from a suitable electrometer (11). Because of its comparative simplicity, the latter method was chosen for the work described in this paper. In the technique developed, current densities of the order of 10^{-6} to 10^{-7} amp/cm² were used. On account of the very small current densities employed, the solutions had to be very carefully freed from extraneous depolarizers, and the electrometer for measuring the potential had to be of a type which would draw negligible current from the electrode. A vacuum tube potentiometer drawing 8×10^{-13} amp was used to measure the electrode potential, and twice-distilled water from an all-Pyrex glass still was used in preparing the solutions. Where necessary the reagents were recrystallized.

The Pyrex glass apparatus, illustrated in Fig. 1, was used to remove oxygen from the solution and electrode vessel. The operation was as follows. The solution was contained in flask *A*. The electrode under study, in the form of a rectangular plate 5 cm² in area, was suspended in *B* on the tungsten hook, *J*, by a wire of the same material as the electrode. Vessels *A* and *B* were evacuated through *C* until the solution boiled under reduced pressure; then by means of tap, *D*, nitrogen, freed from oxygen by passage over reduced copper at 400°C, was admitted into *B*, and bubbled into *A* through the solution. This cycle of operations was repeated three times, after which the solution was blown over into *B* by turning the two-way tap, *D*, to the appropriate setting.

The cap, *E*, was of soda glass with a standard ground-glass joint. Sealed through the top of *E* was a platinum wire which could be used as the auxiliary polarizing electrode. Alternatively, a wire electrode could be suspended from the platinum. The cap, *F*, could be removed and connection made to a saturated calomel reference electrode via an agar jelly-saturated KCl bridge. The purpose of

caps *E* and *F* was to render the system vacuum tight during the evacuation of the apparatus. Taps *H* and *G* were greased only around the ends of the barrel.

The polarizing current was maintained constant within 1 per cent by means of a 90-volt supply and a bank of variable high resistors. Electrode potentials were measured against a saturated calomel reference electrode, and all potentials were recorded on the saturated calomel scale. A single polarization experiment took about 40 minutes; for most of the curves, the potential was recorded every minute. Where more detail was required, more frequent readings were taken, or smaller current densities were used. The current circuit was insulated throughout by polystyrene, and the glass surfaces of the apparatus were proofed against leakage by rings of polystyrene painted on from a benzene solution.

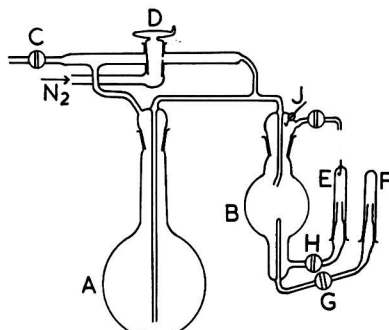


Fig. 1. Apparatus used for (a) removing oxygen from the system, and (b) the polarizing experiments.

RESULTS

Deposition of Metals on the Gold Electrode

A surface treatment, which was found to give a very reproducible gold surface, comprised a degreasing in boiling aqueous caustic soda, an etching in hot aqua regia, and multiple washing in twice-distilled water. In Fig. 2, curve 1 shows the cathodic and anodic polarization of a treated gold electrode in 0.1*N* Na₂CO₃. The slow process revealed on the anodic curve was the discharge of hydroxyl ions, accompanied by the formation of an adsorbed oxide layer on the gold. The final steady potential was the value corresponding to the oxygen overvoltage at the current density used. The arrest on the cathodic curve indicated the reduction of this oxide film, the quantity of electricity involved being 520 microcoulombs/cm². Calculations showed that this film could be no more than one atom thick. This result is in accord with the observations of Armstrong, Himsworth, and Butler (12). The slope of the double-layer portion of the curve indicated a capacity of 70 μf/cm², which is in agreement with the value obtained by Deborin and Ershler (13) for a

gold electrode etched in aqua regia. The deposition of the metals studied in this investigation occurs in the range -0.2 to -0.8 volt on the saturated calomel scale. In this potential range, there is no adsorbed oxide film on the gold surface; in other words, the metals will deposit on a bare gold surface.

In Fig. 2, curves 2, 3, and 4 show typical charging curves obtained with varying concentrations of lead, added as lead acetate. On the cathodic branch of curve 4, the deposition of lead started at -0.4 volt, and, as lead was deposited, the potential fell slowly. When lead equivalent to 500 microcoulombs/cm² had deposited, there was a maximum at -0.775 volt. Then the potential remained steady at -0.76 volt as more lead was deposited. This steady po-

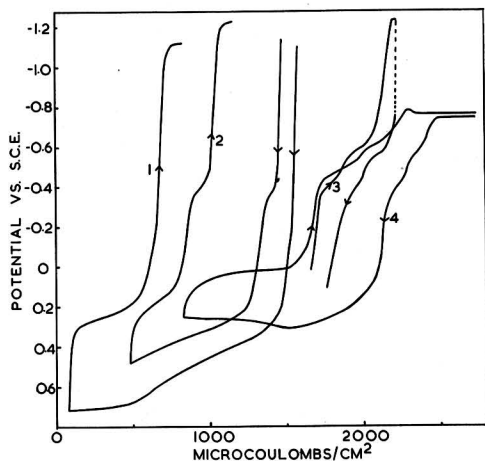
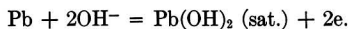


FIG. 2. Charging curves with a gold electrode; current density of 8×10^{-7} amp/cm². Curve 1— $0.1 \text{ Na}_2\text{CO}_3$; curve 2—saturated ($0.04N$) $\text{Ca}(\text{OH})_2$ with 4×10^{-6} mole/liter of lead; curve 3—saturated lime with 4×10^{-6} mole/liter of lead; curve 4— $0.1N \text{ NaOH}$ with 2.5×10^{-3} mole/liter of lead.

tential was the same as that shown by a lead electrode in the same air-free solution, and it corresponded to the potential calculated for the reaction



Using Latimer's data (14), the reversible potential is calculated as -0.756 volt vs. S.C.E. at the pH of the solution (12.8). In view of the uncertainty as to the nature of the solid phase, and errors due to the high liquid junction potentials in such an alkaline solution, the agreement is partly fortuitous. When combined with the observation that the same potential is found with a lead electrode, there can be little doubt that the steady potential does, in fact, correspond to that for the deposition of lead. At higher current densities (with, of course, somewhat

more negative potentials) a visible film of lead can be deposited.

Over a wide range of conditions, the deposition of lead equivalent to 500 microcoulombs/cm² took place before the electrode showed a steady potential corresponding to the reversible lead electrode potential. It is natural to assume that the quantity of lead just mentioned represents approximately a monatomic layer. The value, 500 microcoulombs/cm², pertaining to lead is in good agreement with the value obtained (520) for the adsorption of oxygen on the gold surface. A smooth gold electrode has 1.5×10^{15} atoms/cm², and 500 microcoulombs corresponds to 1.6×10^{15} atoms. The surface of the etched gold will have a greater number of atoms/cm² than this figure calculated for an ideally smooth electrode. Hence, although the lead film is of the order of a monatomic film, it most probably is less than a complete monolayer.

The maximum at -0.775 volt in curve 4 of Fig. 2 suggests a temporary "overvoltage" in the process of the growth of lead crystals. In other words, there is a temporary overvoltage effect which marks the transition from the initial stages of deposition to the steady deposition at the reversible electrode potential. This phenomenon is regarded as evidence that there cannot be any discrete crystals of lead growing from active centers on the gold during the initial deposition. There is concordance between this idea and that of a more or less monatomic film as discussed in the previous paragraph.

On anodic polarization, most of the lead was removed at the reversible potential, and the amount corresponding to the last monatomic layer was removed over a potential range up to -0.3 volt.

Both in the deposition and the removal of the monatomic layer, a characteristic kink was observed at approximately the midpoint of the step. Annealing the gold electrode after etching reduced this kink considerably.

The investigation covered the deposition of metal from numerous solutions of lead, the concentrations ranging from 10^{-3} to 10^{-6} molar, and the pH 's from 10 to 13. The potential at which the deposition started varied from -0.3 to -0.4 volt, but there was no obvious regularity. Curves 2 and 3 in Fig. 2 are charging curves in solutions with smaller lead concentrations. In these cases, concentration polarization occurred before massive lead started to deposit. The broken section of curve 3 corresponds to a region where depolarization of the electrode due to the deposition of lead supplemented the anodic polarization current and caused a rapid change in potential.

At lead concentrations below 5×10^{-5} mole/liter, the anodic limit of the curve was the formation of

the oxide film and the evolution of oxygen. With higher concentrations of lead, the formation of the oxide film was interrupted at +0.3 volt, and the oxidation of the lead to the plumbic state occurred. This was accompanied by a drop in potential, as can be seen in curve 4. Prolonged anodic polarization caused a visible film of PbO_2 to form on the electrode. Reduction of the deposit of PbO_2 caused the first arrest on the cathodic section of curve 4.

Fig. 3 contains curves that show the deposition of thallium, antimony, bismuth, and nickel on gold. Curve 1 reveals the deposition of thallium from a 0.1*N* Na_2SO_4 solution containing 5×10^{-5} mole/liter of the thallium, added as Tl_2SO_4 . The deposition of thallium started at -0.2 volt, and over the range to -0.88 volt, thallium equivalent to 250 microcoulombs/cm² was deposited. At -0.88 volt, thallium was deposited at a steady potential. The first stage of thallium deposition is equivalent to the same number of atoms as that involved in the first deposition of lead, and there is a characteristic kink at -0.5 volt on the curve. There is an overvoltage maximum of only 2 mv on the curve, indicating the commencement of the deposition of massive thallium.

Curve 2 shows the deposition of antimony, added as the oxide Sb_2O_3 . The first stage in the process required 500 microcoulombs/cm² over a potential range 0.25 volt more positive than the steady potential corresponding to the deposition of massive antimony. Similar behavior was described by Heyrovsky (15), who studied the deposition and solution of antimony on a mercury electrode with an alternating potential. The slight maximum in the anodic curve at about -0.6 volt presents a puzzling feature. The effect is quite reproducible, and requires further investigation.

The deposition of bismuth from 0.1*N* Na_2CO_3 solution saturated with BiOOH by the addition of $\text{Bi}(\text{NO}_3)_3$ is represented in curve 3. There was an adsorption of bismuth over the potential range -0.2 to -0.5 volt, equivalent to 500 microcoulombs/cm². This is not as great as in the case of lead and thallium, bismuth being a trivalent ion. The potential at which the steady deposition of bismuth occurred corresponds with the potential of -0.53 volt calculated for the reaction,



at the pH of the solution, using Latimer's data (14). In the experiment represented by curve 3, concentration polarization occurred. The broken line indicated the rapid potential change due to the discharge of bismuth ions assisting the polarizing current.

Curve 4 in Fig. 3 represents the deposition of nickel from a 0.1*N* Na_2SO_4 solution containing $1.7 \times$

10^{-4} mole/liter of nickel added as the sulfate. At the current density of 8×10^{-7} amp/cm² used, nickel ions were not discharged until -0.6 volt, and then the discharge was slow. The potential fell to -0.72 volt before nickel deposited at a steady potential. This was 0.11 volt more negative than the potential of -0.61 volt calculated from the Nernst equation. The removal of the deposit gave a more usual type of curve. There was a slight overvoltage in the removal of the massive nickel, but the last layer, equivalent to 500 microcoulombs/cm², was removed over the potential range -0.5 to -0.1 volt. It will be noted that the quantity of electricity required for the anodic curve is considerably less than that required in the corresponding cathodic polarization. This feature is commonly observed in charging curves, but its explanation is obscure. It is perhaps

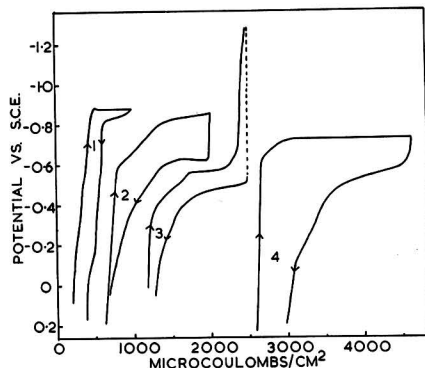


FIG. 3. Gold electrode, current density 8×10^{-7} amp/cm². Curve 1—0.1*N* Na_2SO_4 with 5×10^{-5} mole/liter of thallium; curve 2—0.1*N* Na_2CO_3 with 7×10^{-5} mole/liter of antimony; curve 3—0.1*N* Na_2CO_3 saturated with BiOOH ; curve 4—0.1*N* Na_2SO_4 with 1.7×10^{-4} mole/liter of nickel.

related to the discharge of H^+ ions, giving hydrogen adsorbed on or dissolved in the nickel; the reversible hydrogen potential in the solution is about -0.66 volt. This curve indicates, as Hickling (16) showed, that the slow step in the deposition of nickel is the discharge of the nickel ion; once the nickel ion is discharged, it is bound quite firmly to the gold, as shown by the anodic curve. Reducing the current density increased the potential at which the cathodic curve started to bend; at a current density of 4×10^{-7} amp/cm², the deposition of nickel started at -0.54 volt and the overvoltage was smaller.

Deposition of Lead on Silver

The silver electrode was given a treatment similar to that applied to the gold, except that the etchant used was 1:1 nitric acid. Curve 1 in Fig. 4 shows the charging curve of the silver electrode in 0.1*N*

NaOH. The slow process, represented on the anodic curve from -1.2 to -0.6 volts, corresponds to the adsorption of oxygen on the silver; the arrest on the cathodic curve denotes the reduction of this oxide film. This oxide film, which is stable at such cathodic potentials, exists only in alkaline solutions. Below pH 9, the adsorption of oxygen occurs mainly at a potential about 0.6 volt more noble than that of the above film at the same pH , and, at pH 4, there is no adsorption of oxygen at all, the charging curve being a straight line between the anodic dissolution of silver and the cathodic evolution of hydrogen. This curve (in Fig. 4) confirms the observations of Veselovsky (17), who made an extensive study of the adsorption of oxygen on silver by the method of charging curves.

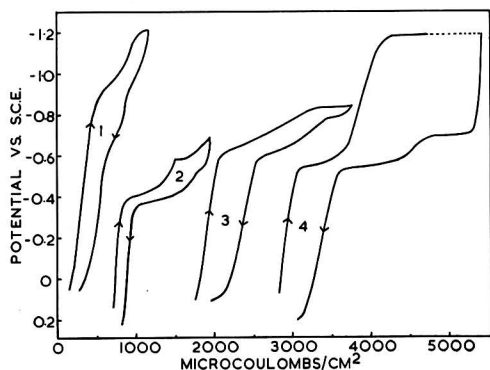


Fig. 4. Silver electrode, current density 8×10^{-7} amp/cm². Curve 1— $0.1N$ NaOH; curve 2— $0.1N$ Na₂SO₄, acidified to pH 4 with 3×10^{-5} mole/liter of lead; curve 3— $0.1N$ NaOH with 10^{-4} mole/liter of lead; curve 4— $0.1N$ Na₂CO₃ with 10^{-5} mole/liter of lead.

Curve 2 in Fig. 4 represents the deposition of lead from a solution at pH 4 containing 3×10^{-5} mole/liter of lead. At this pH , the silver electrode has no oxide film on its surface. Lead equivalent to 750 microcoulombs/cm² was deposited before the potential of the lead electrode calculated from the Nernst equation was reached. Concentration polarization just occurred at this concentration with the current density used. Curve 3 shows the deposition of lead from a $0.1N$ NaOH solution containing 10^{-4} mole/liter of lead. An amount of lead equivalent to $1,000$ microcoulombs/cm² deposited before the reversible lead electrode potential was reached on the cathodic curve. At the pH of a $0.1N$ NaOH solution, the oxide film on silver is not reduced until -0.9 volt, so this lead deposit is on an oxide-covered surface. Curve 4 illustrates the deposition of lead from a $0.1N$ Na₂CO₃ solution containing 10^{-5} mole/liter of the lead. Concentration polarization occurred, and the potential fell to the discharge potential of hydrogen ions. The electrode was left at

this cathodic potential for 3 hours, allowing more lead to deposit, this being indicated by the broken section of the curve. The electrode was then anodically polarized. The lead in excess of the first monolayer was removed at the potential shown by the lead-saturated lead carbonate electrode, then the last layer was removed at a more noble potential and involved an amount equivalent to $1,000$ microcoulombs/cm².

The surface area of silver was not as reproducible as that of gold, and it decreased with time in solution. This change of area was more evident in solutions of low pH than in alkaline solutions, and is attributed to local action currents due to active centers on the silver surface. In acid solutions, the capacity of the double-layer region was $250 \mu\text{f/cm}^2$, and in alkaline solution it was $350 \mu\text{f/cm}^2$. These capacities gave a ratio of 1:1.4 for the surface area of silver in a solution of pH 4, compared with silver in alkaline solutions. If the amount of lead involved in the initial deposition process was taken as a

TABLE I. Data from charging curve experiments on gold and silver

	Gold	Silver
Double-layer capacity, $\mu\text{f/cm}^2$	70	250-350
Microcoulombs/cm ² involved in first stage of deposition of lead . .	500	750-1000

measure of the surface area, the value of 1:1.3 was obtained. This agreement, which was within the limits of the reproducibility of the surface conditions of silver, indicated that the method may prove quite useful. Erbacher (18) used a similar method for obtaining surface areas. He measured the deposition of a radioactive noble metal on a base metal, caused by local action currents. He considered that, when a monatomic layer of the noble metal deposited, the process stopped.

It is of interest to compare the data obtained in the charging curve experiments on gold and silver as shown in Table I. If it is assumed that the quantity of electricity involved in the first stage of deposition indicated the true surface area, then the ratio of the true area of the silver to that of the gold varies from 1.5 to 2, depending on the pH . The ratio deduced from double-layer capacities varies from 3 to 5. These figures suggest that the double-layer capacities obtained for silver are too high. This was also the opinion of Veselovsky (17), who suggested that oxygen adsorption occurred over the entire region of the polarization of silver. However, more experimental work is required before definite conclusions can be drawn about the possible value of this method for comparing surface areas of metals.

DISCUSSION

By suitable preparation of the basis metal, substantial reproducibility of the general form of the curves can be obtained, as shown in Fig. 5. This illustrates the deposition of lead on a gold electrode from 0.1N NaOH containing 2.5×10^{-3} mole/liter of lead acetate, also shown in curve 4, Fig. 2. The initial deposition [1] is followed by removal of the deposit [1A], and finally by a second deposition [2].

Comparing [1] and [2], it will be seen that there is much less agreement for the quantities of electricity involved in the process occurring over the range -0.4 to -0.76 volt. Fig. 5 has been chosen as an example of very poor reproducibility with regard to the quantity of electricity; in general, much closer agreement is obtained. Such variations in quantities may reflect variations in real surface area, or in the area available for deposition of metal. The electrode

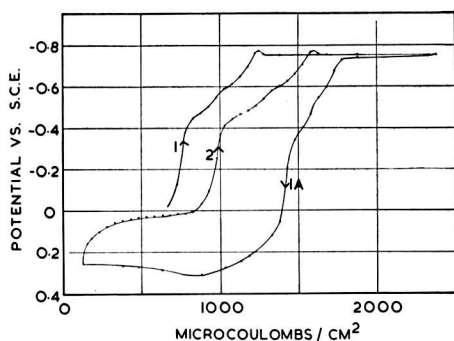


FIG. 5. Deposition of lead [1], followed by removal of lead [1A] and a second deposition [2] from 0.1N NaOH with 2.5×10^{-3} mole/liter of lead.

areas may be compared by measurement of the coulombs required for the production or removal of a well-defined oxide film, such as that on gold. However, it has to be assumed that the area available for the formation of oxide film is identical with that on which metal depositions take place. This uncertainty about surface areas is the main difficulty in the interpretation of results.

There is comparatively little error in the actual measurements of potential and time; the experimental points in Fig. 5 do not represent the actual experimental errors, but have been enlarged for visibility.

A possible source of errors in work of this type is loss of electricity in electrochemical processes other than that being studied. Under this heading come errors due to deposition of metallic impurities, or electrochemical reduction of other substances in solution, such as oxygen. A less obvious source of error is the use of electricity in the reduction of adsorbed oxygen or similar films, or in the formation of

adsorbed hydrogen films. These processes can be observed by charging curves taken in the absence of the metal to be deposited, but it is necessary to insure that the addition of metal does not affect the properties of any such films. This means that the most suitable potential range for following the deposition of a metal is that in which the only process, in the absence of the metal, is the charging of the electrical double layer of the interface. If local action currents exist at the surface of the basis metal, there may be a difference between the applied and true cathodic currents, but it is difficult to assess the possibility of appreciable errors from this effect.

SUMMARY

The results demonstrate clearly the following points.

1. Deposition on an incompletely covered electrode can occur at a potential several tenths of a volt more noble than that calculated from the usual Nernst equation for the reversible electrode potential.

2. The deposition of lead on gold and silver from a 0.1N NaOH solution shows that the "inert" electrode affects the potential at which deposition starts. On gold, the deposition starts 0.2 volt more noble than on silver.

3. The curves for the deposition of lead on silver indicate how the nature of the surface and the oxide films affects the deposition.

The results show that the nature of the deposition varies greatly with the metal being deposited. Thus, the method should be of great value in studying the fundamentals of electroplating and the effects of various addition agents employed by electroplaters to govern the nature of the deposit.

From the detail of the deposition processes revealed by the method of charging curves, it is seen that the technique is superior to others for the study of the early stages of electrodeposition; besides it gives direct information as to the state of the electrode surface on which the deposition is occurring.

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Theory of the Effect of Electrode Resistance on Current Density Distribution in Electrolytic Cells¹

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ABSTRACT

The effect of ohmic resistance of electrodes on current density distribution is shown to depend on the magnitudes of certain dimensionless parameters. For plane parallel electrode systems, exact solution of the problem is obtained in terms of infinite series, which, however, converge rapidly enough to permit practical application. It is demonstrated that, for small interelectrode-electrode length ratio, the assumption of parallel flow is permissible, yielding a convenient expression in closed form for current density distribution, which contains only one parameter.

INTRODUCTION

Methods of predicting the distribution of current over electrode surfaces are of great interest in applied electrochemistry. Qualitative principles of the effects of geometry, polarization, current efficiency, conductance, etc., on current distribution have been elucidated by Foerster (1), Gardam (2), Hoar and Agar (3), among others. Kasper (4) published a series of papers on the effect of geometry on current distribution, including the effect of polarization. Kasper's contribution is distinguished by the use of the exact methods of mathematical physics. Later Wagner (5) presented an excellent mathematical analysis of current distributions on electrodes of triangular wave profile, and on plane electrodes of finite breadth. A critical review of the literature on current distribution problems in electroplating has been presented by Kronsbein (6).

In solving these mathematically complex problems it has been assumed that the electrodes are equipotential, e.g., they are infinitely good conductors. In the following, an attempt is made to clarify under what conditions the electrode can be considered equipotential, and, where the variation of potential along the electrode is not negligible, what effect this boundary condition has on the distribution of current. Due to mathematical difficulties, only those cases where the current distribution is uniform in the absence of terminal effect² are considered.

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² The term "terminal effect" has been used by Kasper (7) to describe the nonequipotential condition of the electrode resulting from ohmic potential drop in the electrode.

DESCRIPTION OF THE MODEL

Fig. 1 illustrates a pair of parallel plane electrodes, the edges being connected by insulating planes normal to the electrode surfaces. This trough is filled with an electrolyte to level $x = 0$. Clearly, this geometry corresponds to that of a linear conductor. The effect of finite electrode resistance on current distribution is considered for this particular cell geometry, assuming the following:

1. The Ohm-Fourier law of conduction is obeyed.
2. Both the electrodes and the electrolyte are homogeneous and isotropic conductors.
3. The electrodes are uniformly thin sheets, the thickness being negligible.
4. The discontinuity of potential at the electrode-solution interface (electrode potential) is a linear function of the current density (linear polarization).
5. The current enters or leaves the system distributed uniformly along lines AB and CD.

The geometric model and the assumptions outlined above imply that this is a two-dimensional problem. Since there is no dependence on z , it is possible to consider arbitrarily the section of the cell between the parallel planes $z = 0$ and $z = 1$.

Symbols

l = length of the electrode, cm.

d = distance between the electrodes, cm.

r_0, r_d = resistance of a 1-cm wide section of the electrode at $y = 0$ and $y = d$, respectively, per unit length in the x direction, ohm.

K = specific conductivity of electrolyte, $\text{ohm}^{-1}\text{cm}^{-1}$.

λ_0, λ_d = dimensionless parameter $\lambda_0 = r_0 Kl$, $\lambda_d = r_d Kl$.

$V(x, y)$ = value of the potential at (x, y) in the cell, volts.

$J(x, y)$ = value of the stream function at (x, y) in the cell, amp/cm.

J_l = total current between $z = 0$ and $z = 1$ cm, amp/cm.

$i(x, 0)$, $i(x, d)$ = current density at the $y = 0$ and $y = d$ electrodes, at x depth, amp/cm².

i_{avg} = average current density = J_l/l , amp/cm².

E_e = equilibrium single electrode potential, volts.

ΔE_p = polarization voltage, representing the departure of electrode potential from E_e , volts.

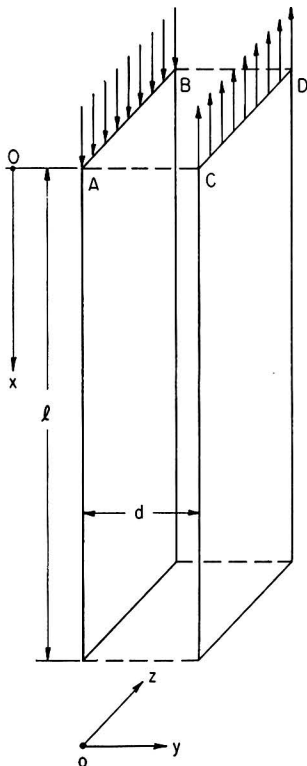


Fig. 1. The geometry of the model

E'_e = hypothetical³ single electrode potential, defined by $E_e + \Delta E_p = E'_e + b \cdot i$, volts.

b_0 , b_d = absolute values of the slopes of the single electrode potential vs. current density curves, assumed to be constants for the interval of current densities $i(0, y)$ to $i(l, y)$ (corresponds to linear polarization), ohm cm².

μ_0 , μ_d = dimensionless parameters, $\mu_0 = \frac{K \cdot b_0}{l}$,

$\mu_d = \frac{K \cdot b_d}{l}$

³ For a more detailed definition of the meaning of E_e , ΔE_p , E'_e , see Reference (5).

ϕ = dimensionless parameter, $\phi^2 = \frac{\lambda_0 + \lambda_d}{\frac{d}{l} + \mu_0 + \mu_d}$

MATHEMATICAL TREATMENT

The problem of finding the distribution of current in this cell is most conveniently solved by introducing the so-called (8) stream function $J(x, y)$. The definition of $J(x, y)$ can be given as follows: if (x_1, y_1) and (x_2, y_2) are parallel lines, then $J(x_2, y_2) - J(x_1, y_1)$ is the current passing through an arbitrary surface through the two. In a medium where no free charges exist, such as the electrolyte, the stream function satisfies Laplace's equation:

$$\frac{\delta^2 J}{\delta x^2} + \frac{\delta^2 J}{\delta y^2} = 0 \quad (I)$$

and the lines $J = \text{constant}$ (streamlines) are orthogonal to the equipotential lines ($V = \text{constant}$). This orthogonality is expressed in the following relation between J and V in the electrolyte:

$$\frac{\delta J}{\delta x} = -K \frac{\delta V}{\delta y} \quad \text{and} \quad \frac{\delta J}{\delta y} = K \frac{\delta V}{\delta x} \quad (II)$$

Equation (II) also contains Ohm-Fourier's law, according to which the current density and the electrical field strength are proportional, with proportionality factor K .

In order to complete the definition of the problem, the boundary conditions to which equation (I) is subjected must be specified. The boundary conditions at $x = 0$ and $x = l$ are very simple: these lines are also streamlines of the current. Since the stream function is determined only up to an additive constant, $J = 0$ may arbitrarily be set at $x = 0$. Let J_l denote the total current entering the electrode at $x = 0, y = 0$; then this is the total current flowing across the electrolyte between $x = 0$ and $x = l$. It follows that the value of the stream function at $x = l$ is J_l . This gives as the first set of boundary conditions:

$$J(0, y) = 0, \quad 0 \leq y \leq d \quad (III)$$

$$J(l, y) = J_l, \quad 0 \leq y \leq d. \quad (IV)$$

The boundary conditions at the electrodes $y = 0$ and $y = d$ form the main difficulty of the problem. We shall treat at once the most general case of terminal effect and polarization at both electrodes (within the limitations set forth by the assumptions in the preceding section).

The combined effect of equilibrium single electrode potential and polarization is a rapid change of potential across a thin layer adjacent to each electrode, from the value in the electrolyte to that in the electrode. To facilitate further developments, imagine a plane in the electrolyte parallel

and immediately adjacent to each electrode. It is customary to describe the position of the plane adjacent to the electrode at $y = 0$ by $y = 0+$ and the position of the plane adjacent to the electrode at $y = d$ by $y = d - 0$.

According to the assumption of linear polarization,⁴ the value of the discontinuity of potential at any point of either electrode is a constant, plus a term proportional to the normal component of the current density at that point. In the electrolyte, the current flows from $y = 0$ to $y = d$. Hence, at the electrode $y = 0$:

$$V(x, 0) - V(x, 0+) = E'_e + b_0 \frac{\delta J(x, 0)}{\delta x} \quad (V)$$

in which $\partial J(x, 0)/\partial x$ is the current density at any point x on the electrode.

The contribution of the terminal effect to the boundary conditions may be obtained as follows. The amount of current which has left the electrode at $y = 0$ between $x = 0$ and $x = x$ is $J(x, 0)$ by definition of the stream function. Since the total current entering the electrode is J_l , the difference $J_l - J(x, 0)$ flows down through the electrode at the point x . If the resistance of the electrode/cm is r_0 , by Ohm's law:

$$\frac{\delta V(x, 0)}{\delta x} = -r_0[J_l - J(x, 0)]. \quad (VI)$$

It is important to remember that J has no discontinuities, so that J and its derivatives may be evaluated either at $y = 0$, or at $y = 0+$.

The combined effect of polarization and terminal effect is obtained after differentiating equation (V) with respect to x and substituting this derivative into equation (VI):

$$\frac{\delta V}{\delta x} = -r_0(J_l - J) - b_0 \frac{\delta^2 J}{\delta x^2}, \quad y = 0+. \quad (VII)$$

Since $y = 0+$ is in the electrolyte, equation (II) may be used to relate $\partial V/\partial x$ to $\partial J/\partial y$. From equations (II) and (VII),

$$\frac{\delta J}{\delta y} = -r_0 K(J_l - J) - b_0 K \frac{\delta^2 J}{\delta x^2}, \quad y = 0 \quad (VIII)$$

in which again all terms may be evaluated at $y = 0$, due to the continuity of J . At the other electrode a similar condition is obtained:

$$\frac{\delta J}{\delta y} = +r_d K(J_l - J) + b_d K \frac{\delta^2 J}{\delta x^2}, \quad y = d. \quad (IX)$$

⁴ The assumption of linear polarization involves the substitution of the polarization voltage vs. current density curve by a straight line, for the interval of current densities appearing in the problem. This approximation may lead to serious errors, if $i_{\max}/i_{\min} \gg 1$. A detailed discussion of the linear polarization assumption has been presented, among others, by Wagner (5).

Due to the relative complexity of the boundary conditions (VIII) and (IX), it has not been possible to obtain a solution in a closed form. However, since both the differential equation (I) and the boundary conditions (III), (IV), (VIII), and (IX) are linear in J and its derivatives, a solution in the form of an infinite series can be obtained.

For the stream function the following series can be written:

$$J(x, y) = J_l \left[\frac{x}{l} + \sum_{n=1}^{\infty} \sin \left(n\pi \frac{x}{l} \right) \left(A_n \text{Sh } n\pi \frac{y}{l} + B_n \text{Ch } n\pi \frac{y}{l} \right) \right]^5 \quad (X)$$

in which the coefficients A_n and B_n have to be determined from the boundary conditions. The first term on the right-hand side of (X), $J_l x/l$, represents a uniform flow, with a density J_l/l . This term would be the solution if there were no terminal effect. The polarization and terminal effects are embodied in the infinite series on the right-hand side of (X).

It can be easily verified that (X) satisfies (I); in fact every term in (X) satisfies (I). The terms in the infinite series have been judiciously chosen such as to satisfy the boundary conditions (III) and (IV); in fact, each term in the series vanishes for $x = 0$ and $x = l$. Of the boundary conditions still to be satisfied, consider (VIII) first. From (X) we obtain by differentiating the terms in the series one by one⁶

$$\frac{\delta J}{\delta y} = J_l \sum_{n=1}^{\infty} \frac{n\pi}{l} A_n \sin n\pi \frac{x}{l}, \quad \text{at } y = 0 \quad (XI)$$

$$\frac{\delta^2 J}{\delta x^2} = -J_l \sum_{n=1}^{\infty} (n\pi/l)^2 B_n \sin n\pi \frac{x}{l} \quad \text{at } y = 0. \quad (XII)$$

Substituting into (VIII) equations (XI) and (XII) together with the value of J at $y = 0$:

$$\sum_{n=1}^{\infty} \left[\frac{n\pi}{l} A_n - r_0 K B_n - b_0 K \left(\frac{n\pi}{l} \right)^2 B_n \right] \sin n\pi \frac{x}{l} = -r_0 K \left(1 - \frac{x}{l} \right). \quad (XIII)$$

At this point, for convenience, the dimensionless quantities are introduced:

$$\lambda_0 = r_0 Kl, \quad \lambda_d = r_d Kl, \quad \mu_0 = \frac{b_0 K}{l}, \quad \mu_d = \frac{b_d K}{l}. \quad (XIV)$$

After substitutions according to (XIV), equation

⁵ The symbols Sh and Ch denote the hyperbolic sine and hyperbolic cosine, respectively.

⁶ The justification of this procedure depends on the uniform convergence of the derived series (9). This behavior can be established after A_n and B_n have been evaluated.

(XIII) reads:

$$\sum_{n=1}^{\infty} [n\pi A_n - (\lambda_0 + n^2\pi^2\mu_0) B_n] \sin n\pi \frac{x}{l} = -\lambda_0 \left(1 - \frac{x}{l}\right) \quad (\text{XV})$$

It is possible to develop $1 - x/l$ into a Fourier series as follows:

$$1 - \frac{x}{l} = \sum_{n=1}^{\infty} \frac{2}{n\pi} \sin n\pi \frac{x}{l}, \quad 0 < x \leq l$$

and substituting this series into the right-hand side of (XV) the coefficients of $\sin n\pi x/l$ on both sides can be compared:

$$n\pi A_n - (\lambda_0 + n^2\pi^2\mu_0)B_n = -\frac{2}{n\pi} \lambda_0, \quad n = 1, 2, \dots \quad (\text{XVI})$$

In a similar manner from (IX):

$$n\pi \left(B_n \operatorname{Sh} n\pi \frac{d}{l} + A_n \operatorname{Ch} n\pi \frac{d}{l} \right) + (\lambda_d + n^2\pi^2\mu_d) \left(A_n \operatorname{Sh} n\pi \frac{d}{l} + B_n \operatorname{Ch} n\pi \frac{d}{l} \right) \quad (\text{XVII}) \\ = \frac{2}{n\pi} \lambda_d \quad n = 1, 2, \dots$$

Equations (XVI) and (XVII) are solved now for A_n and B_n :

$$A_n = \frac{2}{n\pi} \frac{1}{C_n} \left[\lambda_d(\lambda_0 + n^2\pi^2\mu_0) - n\pi\lambda_0 \operatorname{Sh} n\pi \frac{d}{l} - \lambda_0(\lambda_d + n^2\pi^2\mu_d) \operatorname{Ch} n\pi \frac{d}{l} \right] \quad (\text{XVIII})$$

$$B_n = \frac{2}{n\pi} \frac{1}{C_n} \left[n\pi\lambda_d + \lambda_0(\lambda_d + n^2\pi^2\mu_d) \operatorname{Sh} n\pi \frac{d}{l} + n\pi\lambda_0 \operatorname{Ch} n\pi \frac{d}{l} \right] \quad (\text{XIX})$$

with the abbreviation:

$$C_n = [\lambda_0\lambda_d + n^2\pi^2(1 + \lambda_0\mu_d + \lambda_d\mu_0) + n^4\pi^4\mu_0\mu_d] \quad (\text{XX})$$

$$\operatorname{Sh} n\pi \frac{d}{l} + [n\pi(\lambda_0 + \lambda_d) + n^3\pi^3(\mu_0 + \mu_d)] \operatorname{Ch} n\pi \frac{d}{l}.$$

Substitution of (XVIII) and (XIX) into equation (X) gives the current distribution in the electrolyte, which can be expressed in the form:

$$\frac{J(x, y)}{J_l} - \frac{x}{l} = \sum_{n=1}^{\infty} \frac{2}{n\pi} \left(\sin n\pi \frac{x}{l} \right) \frac{1}{C_n} \left[\lambda_d(\lambda_0 + n^2\pi^2\mu_0) \operatorname{Sh} n\pi \frac{y}{l} + \lambda_0(\lambda_d + n^2\pi^2\mu_d) \operatorname{Sh} n\pi \frac{d-y}{l} + n\pi\lambda_d \operatorname{Ch} n\pi \frac{y}{l} + n\pi\lambda_0 \operatorname{Ch} n\pi \frac{d-y}{l} \right] \quad (\text{XXI})$$

It is apparent that this expression is invariant under the interchange of the subscripts 0 and d , and simultaneous interchange of y and $d - y$, which reflects the irrelevance of the special choice of the coordinate system.

Of special interest is the current distribution at the electrodes. At the electrode $y = 0$:

$$\frac{J(x, 0)}{J_l} = \frac{x}{l} + \sum_{n=1}^{\infty} \frac{2}{n\pi} \left(\sin n\pi \frac{x}{l} \right) \frac{1}{C_n} \left[n\pi\lambda_d + \lambda_0(\lambda_d + n^2\pi^2\mu_d) \operatorname{Sh} n\pi \frac{d}{l} + n\pi\lambda_0 \operatorname{Ch} n\pi \frac{d}{l} \right] \quad (\text{XXII})$$

The current distribution at $y = d$ is obtained from (XXII) by interchanging the subscripts 0 and d .

The solution represented by equation (XXII) simplifies considerably if polarization and terminal effect are restricted to one electrode only. If $\lambda_d = 0$, and $b_d = 0$, we obtain for the $y = 0$ electrode:

$$\frac{J(x, 0)}{J_l} = \frac{x}{l} + 2 \sum_{n=1}^{\infty} \left(\sin n\pi \frac{x}{l} \right) \frac{1}{n\pi + \frac{\mu_0 n^3 \pi^3}{\lambda_0} + \frac{n^2 \pi^2}{\lambda_0} \operatorname{Th} \pi n \frac{d}{l}} \quad (\text{XXIII})$$

where Th denotes the hyperbolic tangent.

The distribution at the $y = d$ electrode is obtained if one divides the infinite series in (XXIII) term by term by $\operatorname{Ch} n\pi \frac{d}{l}$:

$$\frac{J(x, d)}{J_l} = \frac{x}{l} + 2 \sum_{n=1}^{\infty} \left[\left(\sin n\pi \frac{x}{l} \right) \frac{1}{n\pi + \frac{\mu_0 n^3 \pi^3}{\lambda_0} + \frac{n^2 \pi^2}{\lambda_0} \operatorname{Th} n\pi \frac{d}{l}} \right] \cdot \frac{1}{\operatorname{Ch} n\pi \frac{d}{l}} \quad (\text{XXIV})$$

In the absence of polarization effects, and with terminal effect only at the $y = 0$ electrode, we obtain from (XXIII):

$$\frac{J(x, 0)}{J_l} = \frac{x}{l} + 2 \sum_{n=1}^{\infty} \left(\sin n\pi \frac{x}{l} \right) \frac{1}{n\pi + \frac{n^2 \pi^2}{\lambda_0} \operatorname{Th} n\pi \frac{d}{l}} \quad (\text{XXV})$$

and at $y = d$

$$\frac{J(x, d)}{J_l} = \frac{x}{l} + 2 \sum_{n=1}^{\infty} \left[\left(\sin n\pi \frac{d}{l} \right) \frac{1}{n\pi + \frac{n^2 \pi^2}{\lambda_0} \operatorname{Th} n\pi \frac{d}{l}} \right] \cdot \frac{1}{\operatorname{Ch} n\pi \frac{d}{l}} \quad (\text{XXVI})$$

Simplified Treatment

Assuming that the flow across the cell is uni-directional, i.e., J is independent of y , irrespective of the potential drop in the electrode in direction x , the differential equation

$$\frac{d^2 J}{dx^2} = \frac{1}{l^2} \phi^2 [J_l - J(x)] \tag{XXVII}$$

with the boundary conditions:

$$\begin{aligned} J(0) &= 0 \\ J(l) &= J_l \end{aligned} \tag{XXVIII}$$

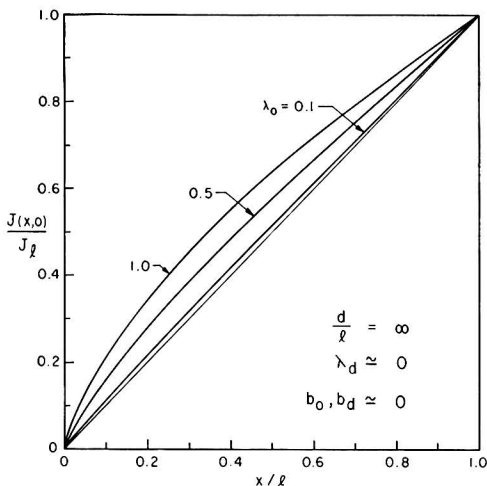


FIG. 2. The effect of λ on current distribution. The electrodes are far apart. [The effect of polarization is not considered. Electrode at (d) is a good conductor.]

yields the solution:

$$\frac{J(x)}{J_l} = 1 - \frac{\text{Sh } \phi \left(1 - \frac{x}{l}\right)}{\text{Sh } \phi} \tag{XXIX}$$

For the current density by differentiation of (XXIX):

$$\frac{i(x)}{i_{\text{avg}}} = \phi \frac{\text{Ch } \phi \left(1 - \frac{x}{l}\right)}{\text{Sh } \phi} \tag{XXX}$$

Solution (XXIX) does not satisfy the differential equation (I). However if $d/l \ll 1$ the streamlines should be very close to parallel, therefore (XXIX) may be a good approximation of the exact solution under these conditions. To investigate the limits of applicability, one can expand (XXIX) in a Fourier

⁷ A similar solution for the current distribution in concentric cylindrical electrode systems has been presented by Weisselberg and staff (10).

series:

$$\begin{aligned} \frac{J(x)}{J_l} - \frac{x}{l} &= \sum_{n=1}^{\infty} \frac{2}{n\pi} \sin n\pi \frac{x}{l} \frac{1}{1 + \frac{n^2 \pi^2}{\phi^2}}, \\ 0 &\leq x \leq l \end{aligned} \tag{XXXI}$$

For x/l not $\ll 1$, the number of terms in the series which contribute appreciably to the value of the series is not large. If $d/l \ll 1$, $n\pi d/l \ll 1$ for all the terms that have to be considered. The quantities $n\pi d/l$, $n\pi y/l$, and $n\pi(d - y)/l$ appear as arguments of the hyperbolic sine and cosine. Under the above mentioned conditions, the Sh may be replaced by

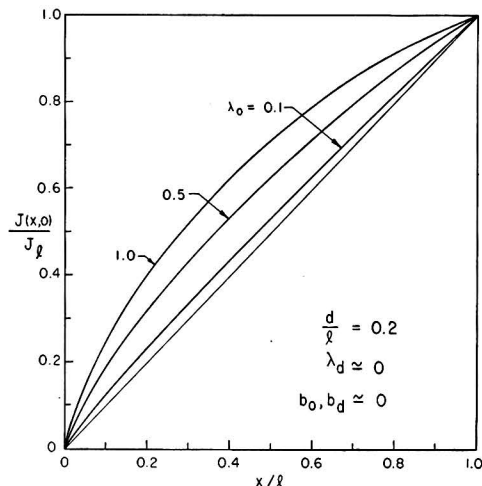


FIG. 3. The effect of λ on current distribution. The electrodes are close together. [The effect of polarization is not considered. Electrode at (d) is a good conductor.]

its argument, and Ch by 1. Carrying out this approximation, it can be shown that equation (XXII) reduces to (XXXI), provided $\lambda_0 + \lambda_d$ is not $\gg 1$ and $\mu_0 + \mu_d$ is not $\gg 1$. Therefore, equation (XXX) may be used to calculate current density distributions under these conditions.

RECOMMENDATIONS FOR NUMERICAL SOLUTIONS

Numerical solutions obtained for the purposes of illustration were restricted to cases where the electrode at $y = d$ has no terminal effect and its polarization is constant. This restriction was applied purely to shorten the time necessary for obtaining sufficient qualitative information about the behavior of the current distribution function. For $d/l \ll 1$, however, examples given here include the possible effect of polarization and terminal effect at both electrodes.

The solution of differential equation (I) has been obtained in terms of the stream function. The derivative of $J(x, 0)$ or $J(x, d)$ with respect to x gives the current density distribution at the respective elec-

trodes. Inspection of equation (XXII) reveals that the derived series converges much more slowly than the original series. For this reason some of the illustrative numerical solutions have been evaluated

length dimension of the cell (for small d/l the characteristic length is d , for $d/l > 1$ it is l), unless $\lambda_0 \gg 1$, the derived series obtained from equation (XXII) will be dominated by a series in which the

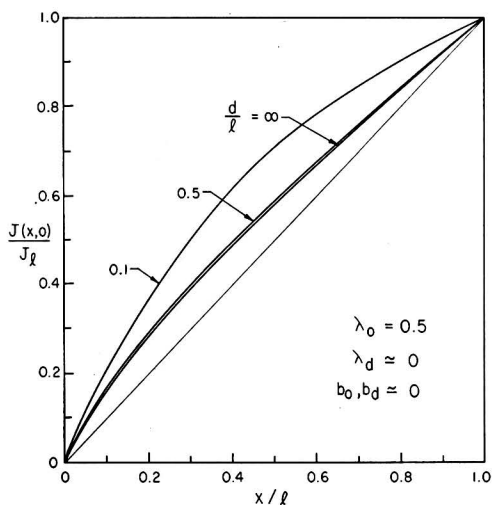


FIG. 4. The effect of electrode separation on current distribution. [The effect of polarization is not considered. Electrode at (d) is a good conductor.]

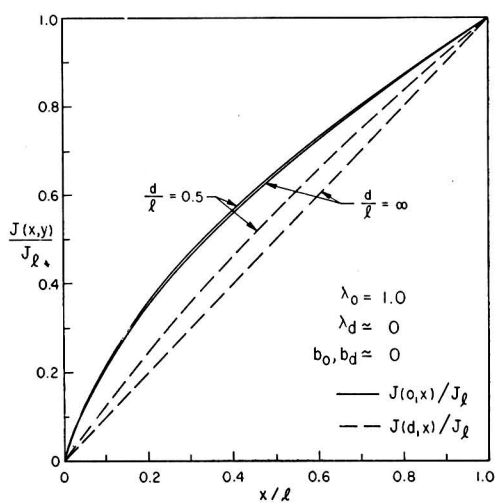


FIG. 6. Comparison of current distribution at the high resistance (0) and low resistance (d) electrodes. The electrodes are far apart. (Polarization effects are neglected.)

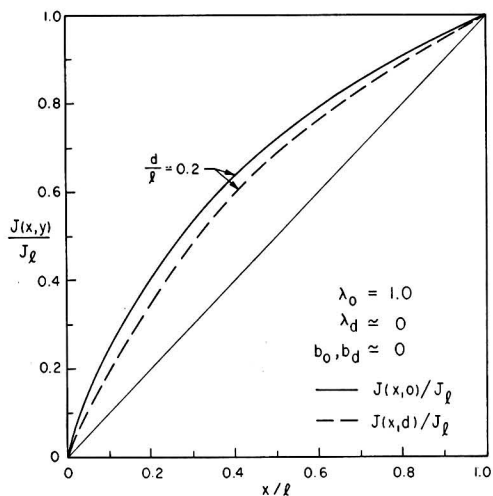


FIG. 5. Comparison of current distribution at the high resistance (0) and low resistance (d) electrodes. The electrodes are close together. (Polarization effects are neglected.)

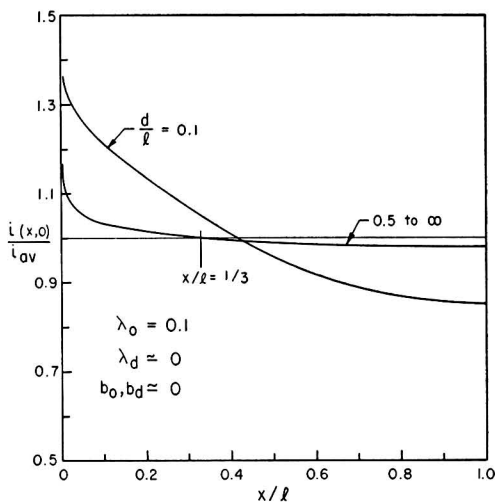


FIG. 7. The effect of electrode separation on current distribution. [The effect of polarization is not considered. Electrode at (d) is a good conductor.]

in terms of the stream function. Graphical differentiation of these $J(x, 0)/J(l)$ vs. x/l curves can provide reasonably correct current density distribution values. However, if the polarization term $K(\mu_0 + \mu_d)$ is larger than, or comparable to, the characteristic

terms are proportional to $1/n^2$, which assures rapid convergence. This property of the solution is especially clearly shown by equation (XXIII). The condition $\lambda_0 \gg 1$ is not anticipated to occur frequently in practical problems.

The values of the stream function in the absence

of polarization, and terminal effect at only $y = 0$, have been evaluated by using equation (XXV) (Fig. 2, 3, 4, 5, and 6). For the region $0.1 < x/l < 1$ it was sufficient to consider only the first six terms

tained:

$$\frac{2\lambda_0}{\pi} \left[\frac{\sin 10\pi \frac{x}{l}}{10\pi} - \frac{x}{l} \text{Ci} \left(10\pi \frac{x}{l} \right) \right] \quad (\text{XXXII})$$

in which Ci denotes the cosine integral (11).

For λ_0 smaller than approximately 1, and $d/l > 0.7$ (Fig. 7) the series in equation (XXV) can be

TABLE I. Values of $i(x)/i_{av}$ as a function of the terminal effect parameter ϕ , calculated from equation (XXX)

x/l	ϕ					
	0.2	0.4	0.6	0.8	1.0	1.2
0	1.0133	1.0528	1.1173	1.2047	1.313	1.4394
0.1	1.0095	1.0376	1.0831	1.1445	1.2194	1.3054
0.2	1.0061	1.0241	1.053	1.0916	1.138	1.1903
0.3	1.0031	1.0122	1.0268	1.0458	1.068	1.0923
0.4	1.0005	1.002	1.0042	1.0066	1.0087	1.010
0.5	0.9983	0.9934	0.9852	0.9738	0.9595	0.9424
0.6	0.9965	0.9863	0.9697	0.9473	0.9199	0.8882
0.7	0.9951	0.9808	0.9577	0.9268	0.8895	0.8470
0.8	0.9941	0.9769	0.9492	0.9123	0.8680	0.8179
0.9	0.9935	0.9746	0.9441	0.9037	0.8552	0.8007
1.0	0.9933	0.9738	0.9424	0.9008	0.8509	0.7949

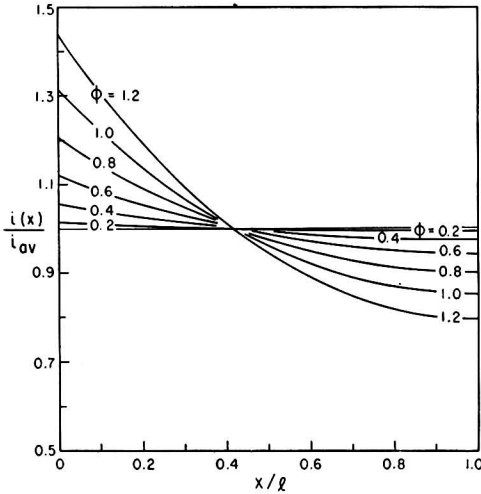


FIG. 8. Current density distribution as a function of ϕ . (Approximate treatment. Polarization and terminal effect at either or both electrodes.)

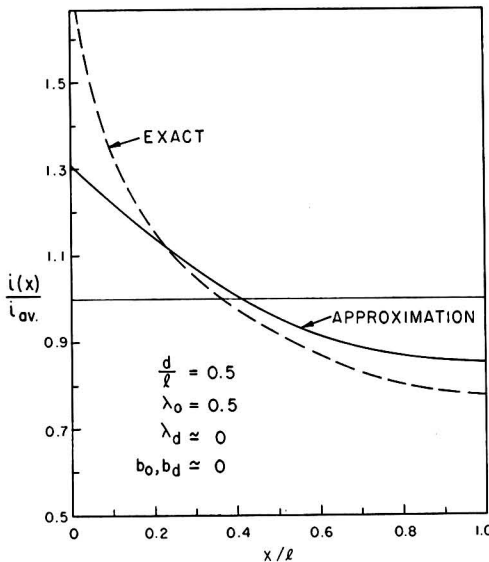


FIG. 9. Comparison of the exact and approximate solutions. The electrodes are at medium distance.

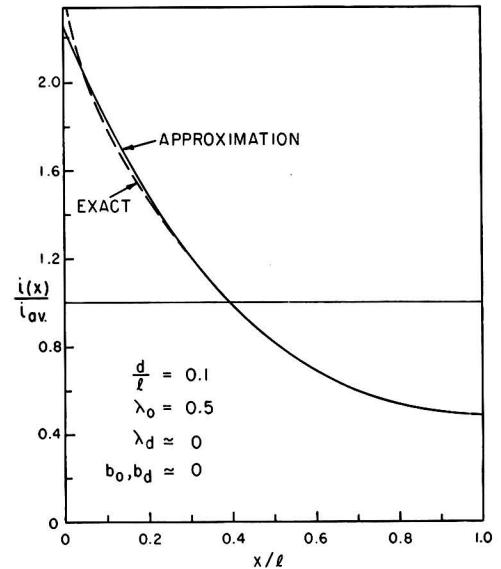


FIG. 10. Comparison of the exact and approximate solutions. The electrodes are close together.

of the series. For $x < 0.1$, however, the convergence is very slow; therefore an approximate value of the series was obtained by adding up the first 10 terms, and replacing the remaining series by an integral, for which the following approximate value was ob-

well approximated by:

$$2\lambda_0 \sum_{n=1}^{\infty} \frac{\sin n\pi \frac{x}{l}}{n^2\pi^2} \quad (\text{XXXIII})$$

The derived series, $\sum_{n=1}^{\infty} 1/n\pi \cos n\pi x/l$ is expressible in closed form (12), and this gives:

$$\frac{i(x, 0)}{i_{avg}} = 1 - \frac{2\lambda_0}{\pi} \ln \left(2 \sin \frac{\pi x}{2l} \right) \quad (\text{XXXIV})$$

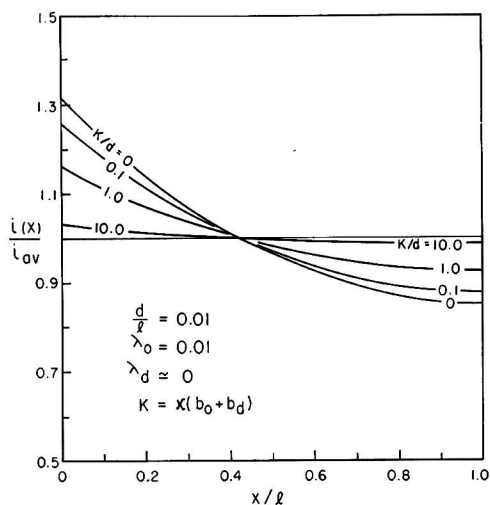


FIG. 11. The effect of polarization on the current distribution. (Approximate treatment. Polarization and terminal effect at either or both electrodes.)

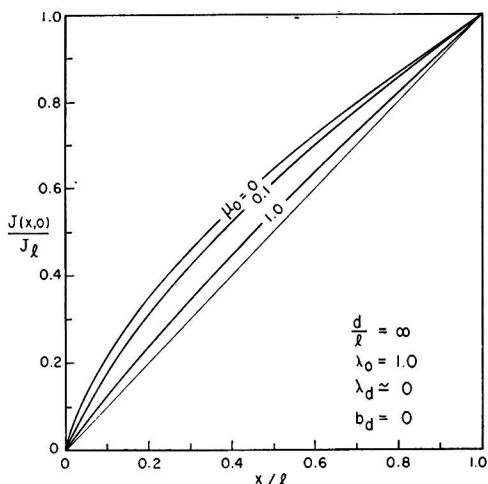


FIG. 12. The effect of polarization on the current distribution. The electrodes are far apart. [No terminal effect and no polarization at the electrode at (d).]

which for small x/l simplifies to:

$$\frac{i(x, 0)}{i_{avg}} = 1 - \frac{2\lambda_0}{\pi} \ln \pi \frac{x}{l} \quad (\text{XXXV})$$

The most important simplification in numerical problems can be realized in the region $d/l < 0.05$, and $\lambda_0 + \lambda_d < 1$. As shown in the previous section

by equations (XXII) and (XXXI) the assumption of unidirectional flow becomes acceptable in this region; therefore, the very convenient closed form expression, equation (XXX), can be used to compute the current density distribution. Significant deviations from the results obtainable by equation (XXII) can only be anticipated in the region $0 \leq x/l < 0.1$. Even in this region the deviation from the exact solution becomes negligible if $\mu_0 + \mu_d/d$ is not $\ll 1$. Values of i_x/i_{avg} vs. x/l have been calculated (Table I) and plotted (Fig. 8) for $\phi = 0.2, 0.4, 0.6, 0.8, 1.0$, and 1.2 . Deviations between the approximate solution and the exact solution are illustrated by Fig. 9 and 10.

The current distribution over the electrode at $y = d$ which has no appreciable resistance can be evaluated easily by the series solution (XXIV) or (XXVI). Convergence is much faster in this case, because of the Ch term in the denominator. Equation (XXVI) has been applied in evaluating the data for Fig. 5 and 6.

DISCUSSION AND CONCLUSION

The geometry chosen and the simplifying physical assumptions impose a restriction on the immediate practical value of this mathematical treatment.

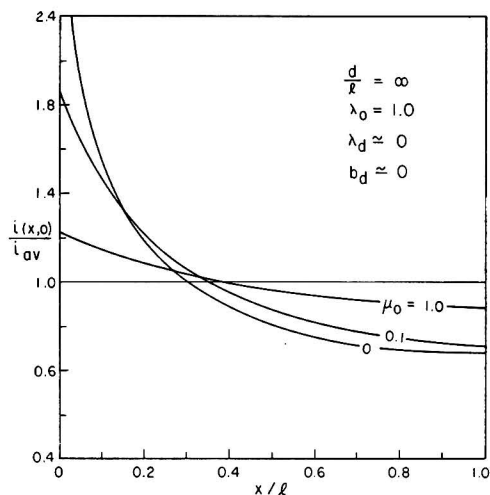


FIG. 13. The effect of polarization on the current distribution. The electrodes are far apart. [No terminal effect and no polarization at the electrode at (d).]

Nevertheless, useful deductions may be based on the results presented, for models less well defined or involving more complicated boundary conditions.

As shown by the mathematical solutions, the current density distribution at the electrodes depends on the magnitude of the terminal effect parameter, λ , of the ratio of electrode separation to electrode

length (d/l), and of the ratio of electrolyte conductivity K times the polarization constant b to the characteristic length dimension of the cell, which is d or l . Inspection of the solutions [equations (XXII), (XXIII), (XXV), and (XXX)] and evaluation of a large number of numerical problems resulted in the following conclusions:

(A) *Dependence on λ 's.* The magnitude of these parameters increases with conductivity of the electrolyte and with resistance of the electrode. Consequently, the nonuniformity of current density distribution increases with increasing λ 's. This fact is illustrated by Fig. 2, 3, and 8.

(B) *Dependence on electrode separation.* Since the resistance of the electrolyte increases with separation for any given electrode length l , a decrease in terminal effect is anticipated with increasing inter-electrode distance for a given λ_0 and l . For d/l smaller than approximately 0.05, the current distribution becomes a unique function of the parameter ϕ . Numerical results show that $i(0)/i(l) < 1.01$, if $\phi < 0.1$; therefore, this value of ϕ may be recommended as the lower limit for considering the effect at all. As d/l is increased beyond about 0.1, the validity of the approximate solution [equation (XXX)] breaks down (Fig. 9 and 10). It is of interest to note that the distribution does not show a dependence on the separation if d/l is increased beyond about 0.7. Beyond this distance ratio the electrode behaves as if it were not affected by the position of the opposite electrode. [The approximate solution, (equation (XXX)), predicts a continuous decrease in nonuniformity with increasing d/l , with uniform distribution for $d/l = \infty$.]

(C) *The effect of polarization* is expected to decrease the nonuniformity in current distribution caused by the terminal effect. As shown previously by Kasper (5), Hoar and Agar (3), and particularly clearly by Wagner (6), not the absolute magnitude of polarization voltage, but its rate of change with current density (characterized by b , the slope) should determine its effect on current distribution. More precisely the absolute magnitude of the parameters μ (defined under Symbols) should serve as an indication whether polarization effects are to be taken into account. This point is illustrated by Fig. 8, 9, and 11. For $d/l \ll 1$, the effect of polarization may be considered to be that of a resistor in series with the electrolyte. In this region, polarization effects become appreciable if $\mu_0 + \mu_d$ is not much smaller than d/l , or in other words $K(b_0 + b_d)/d$ not $\ll 1$.

Equation (XXIII) indicates that, in the absence of polarization, at $x = 0$ (entrance line of current)

the current density is infinite. However, with polarization, the derived series converges even at $x = 0$ (the terms being dominated by $1/n^2$). Therefore, with polarization, even at the entrance line of the current, the current density is finite (Fig. 12 and 13).

(D) *Distribution over the "opposite" electrode.* Equation (XXII) permits the evaluation of current distributions over both electrodes irrespective of whether either or both of the electrodes have appreciable resistances. Equations (XXIII) and (XXIV) are restricted to the case when the "opposite" electrode is an infinitely good conductor. Since this case is of considerable practical importance, an investigation of the behavior of the current distribution function at the electrode at $y = d$ is desirable. Equations (XXIV) and (XXVI) represent the stream function at $y = d$ with $\lambda_d = 0$ and $b_d = 0$. As can be expected, in both cases the current distribution is more uniform at $y = d$, than at $y = 0$. The current density is finite at the entrance line of current even in the absence of polarization (the derived series is dominated by $\sum_{n=1}^{\infty} 1/n \operatorname{Ch} n\pi(d/l)$). For $d/l \ll 1$ the distribution may be considered to be identical to that at the $y = 0$ electrode. With increasing d/l for a fixed λ_0 , the distribution at $y = d$ becomes more and more uniform, attaining uniformity for $d/l = \infty$. It should be noted here that the approximate solution which is applicable only for $d/l \ll 1$ fails to predict this behavior.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Heats of Formation and Entropies of HS⁻ and S⁻. Potential of Sulfide-Sulfur Couple¹

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ABSTRACT

The heat of neutralization of H₂S solutions by NaOH was measured at 25°C for various mole ratios of NaOH to H₂S. These data, with the two dissociation constants of H₂S, allow calculation of the free energies, heats of formation, and the partial molal entropies of S⁻ and HS⁻. The results for S⁻ and HS⁻ are, respectively: ΔF⁰ = 20.6 and 3.00 kcal, ΔH⁰ = 7.8 and -4.10 kcal, and $\bar{S}^0 = -4$ and 15.0 entropy units (eu). The potential of the S⁻ - S couple is 0.447 volt.

INTRODUCTION

The value of \bar{S}_S^0 found in the National Bureau of Standards tables is 5 eu (1). This appears to be considerably too positive for a monatomic, dinegative ion (2). The value is based on the second dissociation constant of H₂S, K^{II} , measured by Kubli (3), and on studies of the heat of H₂S neutralization by several early investigators (4-6). Interpretation of the early thermal data is uncertain because of the high ionic strengths necessarily employed and a lack of reliable activity coefficients for S⁻ and HS⁻.

K^{II} has recently been determined spectrophotometrically over a range of low ionic strengths (7). Thus it appeared desirable to utilize modern calorimetric techniques for a study of the heat of neutralization over a wide range of S⁻ to HS⁻ mole ratios. One can then combine the results of such heat measurements with the data of Konopik and Leberl (7) and obtain more reliable values for the thermodynamic functions of S⁻ and HS⁻.

EXPERIMENTAL

The calorimeter used in this investigation has been previously described (8, 9). All heats were measured at 25.0° ± 0.5°C and are reported in terms of the defined calorie (1 cal = 4.1840 abs joules). The uncertainty in the measured heats is ±0.3 cal. Samples of concentrated NaOH solutions were contained in paraffin-coated, small glass bulbs, and were introduced into the calorimetric solutions by shattering the bulbs with a glass rod.

A 50 per cent stock solution of NaOH, prepared from Baker and Adamson reagent grade pellets, was filtered through glass wool to remove Na₂CO₃, and stored in a paraffin-coated container. Before each run, the NaOH was filtered again through glass

wool and, after appropriate dilution, was transferred immediately to a stoppered, waxed weight buret. A weighed portion of this solution was then added to the sample bulb. The remainder was analyzed by adding a weighed amount of the solution to a known excess of standard HClO₄ and by titrating with standard NaOH to the bromthymol blue end point. Tests on the calorimetric solutions with Ba(NO₃)₂ after several runs revealed only traces of carbonate.

TABLE I. *Experimental results*

(A = moles of H₂S, B = moles of NaOH, C = moles of water in the calorimeter before breaking the sample bulb, D = moles of water in sample bulb, Q = heat evolved in calories, and d = density of the resulting solution at 25°C in g/ml.)

Run	A × 10 ²	B × 10 ²	C	D × 10 ²	Q	d
1	1.399	1.708	60.68	13.21	117.7	0.997
2	1.593	1.909	60.07	4.40	217.6	0.997
3	1.698	2.550	60.88	5.79	258.9	0.997
4	1.674	2.817	60.75	6.38	272.5	0.997
5	1.716	3.793	61.24	8.62	321.2	0.997
6	1.818	4.257	61.44	9.67	351.1	0.998
7	1.522	5.345	60.83	39.49	144.1	0.998
8	1.670	7.001	60.17	49.90	168.6	1.000
9	1.069	6.657	60.50	49.95	108.4	0.999
10	1.550	8.128	61.12	60.91	152.0	1.000
11	1.216	8.640	60.77	64.69	125.9	1.000

An aqueous solution of H₂S was prepared before each run from purified (10), commercial grade H₂S, and a weighed amount of this solution was added to the calorimeter. After the calorimetric run, the resulting Na₂S-NaHS-NaOH solution was analyzed for total sulfide iodimetrically (11).

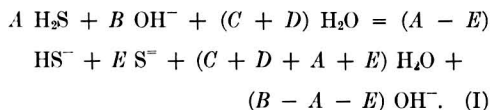
The density of the calorimetric solution—necessary for the calculation of the concentrations of all species present—was measured immediately after each run with calibrated 25 and 50 ml pipets.

The experimental results are presented in Table I.

¹ Manuscript received April 7, 1953.

CALCULATIONS AND DISCUSSIONS

The complete equation for the calorimetric reaction is assumed to be:



Thus, to interpret properly the heat data it is necessary to know the concentrations of all species present after the reaction. Since there is a discrepancy in the K^{II} values reported in the recent studies by Kubli (3), and Konopik and Leberl (7), the pH measurements of both authors were critically re-examined. Both sets of data were found to be consistent upon eliminating Kubli's assumption that activity of OH⁻ equals concentration of OH⁻. All the data were placed on an extended Debye-Hückel plot

TABLE II. *Experimental results*

(E = moles of S⁻ present after reactions; Q 's are given in calories.)

Run	pK_u^{II} (25°C)	$E \times 10^3$	Q'	Q''	Q'''
1	12.69	0.549	4.4	0.1	0.9
2	12.68	0.642	90.2	0.1	1.1
3	12.64	1.803	122.3	0.3	1.6
4	12.62	2.382	135.7	0.4	1.7
5	12.57	4.287	181.9	0.8	2.5
6	12.54	5.250	204.2	1.0	2.8
7	12.49	6.522	17.2	1.3	3.9
8	12.40	9.261	26.0	2.0	5.5
9	12.43	6.088	20.0	1.3	5.6
10	12.36	9.749	24.5	2.2	6.8
11	12.35	8.193	26.0	1.9	7.8

from which it was possible to obtain a pK_u^{II} ($pK_u^{\text{II}} = -\log K_u^{\text{II}}$) value for each calorimetric run. K_u^{II} is not a true equilibrium constant, but a function of ionic strength, and is defined as:

$$K_u^{\text{II}} = \frac{a_{\text{H}^+}(\text{S}^-)}{(\text{HS}^-)} \quad (\text{II})$$

where () refers to moles/liter and a_{H^+} = activity of H⁺.

Since the measurements of Kubli, and Konopik and Leberl were made at 20°C, it was necessary to convert their results to 25°C. The true equilibrium constant, K^{II} , is related to K_u^{II} by:

$$K^{\text{II}} = K_u^{\text{II}} \frac{f_{\text{S}^-}}{f_{\text{HS}^-}} \quad (\text{III})$$

where f_{S^-} and f_{HS^-} refer to the respective activity coefficients. Assuming ΔH^0 of the second dissociation step to be constant over the 5°C temperature range, one can calculate K^{II} at 25°C from the

van't Hoff equation. Then, also assuming that the activity coefficient ratio is constant over the same temperature range, we are able to calculate K_u^{II} at 25°C (Table II). This calculation was done by successive approximations, using first the old heat data, and then correcting with that obtained in this work.

To calculate the concentrations of all species present after reaction, we utilize equation (II), total sulfide concentration, initial NaOH concentration, and the following relationships:

$$(\text{Na}^+) = (\text{OH}^-) + (\text{HS}^-) + 2(\text{S}^-) \quad (\text{IV})$$

$$a_{\text{H}^+} = \frac{1.008 \times 10^{-14}}{(\text{OH}^-)f_{\text{OH}^-}} \quad (\text{V})$$

The activity coefficients of OH⁻, f_{OH^-} , were calculated from Kielland's equation (12). These values were checked against the experimental mean activity coefficients of NaOH (13) and gave very good agreement over the ionic strength range of our experiments ($\mu = 0.01$ to 0.09).

To obtain standard state values, the experimentally observed heats were corrected to infinite dilution for all species. Utilizing the principle of ionic strength, we assume, for example, the heat of dilution of NaOH at $\mu = 0.1$ equals the heat of dilution for 0.1M NaOH. Then neglecting the H₂S heat of dilution, approximating that of NaHS as equal to that of NaOH, and that of Na₂S as equal to that of Na₂SO₄, we define:

Q' = heat evolved for B moles NaOH in D moles of H₂O to infinite dilution (VI)

Q'' = heat evolved for E moles Na₂SO₄ in ionic strength μ to infinite dilution (VII)

Q''' = heat evolved for $(B - 2E)$ moles NaOH in ionic strength μ to infinite dilution (VIII)

$$Q^0 = Q - Q' + Q'' + Q''' \quad (\text{IX})$$

The above dilution heats were obtained from the National Bureau of Standards tables for the heats of formation of NaOH and Na₂SO₄ (1). For the more concentrated NaOH solutions, the heats of dilution were experimentally determined and were found consistent with those calculated from the Bureau of Standards data. The observed heats of formation for the concentrated solutions are:

$$\begin{aligned} &.1 \text{ mole NaOH in } 2.264 \text{ moles H}_2\text{O} & \Delta H_f &= -107.409 \text{ kcal} \\ &1 \text{ mole NaOH in } 2.256 \text{ moles H}_2\text{O} & \Delta H_f &= -107.397 \text{ kcal} \end{aligned}$$

In Table II are found the results of the above calculations.

In order to obtain the standard heats of formation of S^{2-} and HS^- ($\Delta H_{S^{2-}}^0$ and $\Delta H_{HS^-}^0$), we make use of the following equation:

$$-Q_1^0 = (A - E)\Delta H_{HS^-}^0 + E\Delta H_{S^{2-}}^0 + (A + E)\Delta H_{H_2O}^0 - (A + E)\Delta H_{OH^-}^0 - A\Delta H_{H_2S_{aq}}^0 \quad (X)$$

Rearranging gives:

$$Y = \Delta H_{S^{2-}}^0 - \left(\frac{E}{A - E}\right) + \Delta H_{HS^-}^0 \quad (XI)$$

where:

$$Y = -\frac{Q_1^0}{A - E} + \Delta H_{H_2S_{aq}}^0 \left(\frac{A}{A - E}\right) + \frac{A + E}{A - E} (\Delta H_{OH^-}^0 - \Delta H_{H_2O}^0) \quad (XII)$$

Thus, in Fig. 1, a plot of Y vs. $E/(A - E)$ gives a

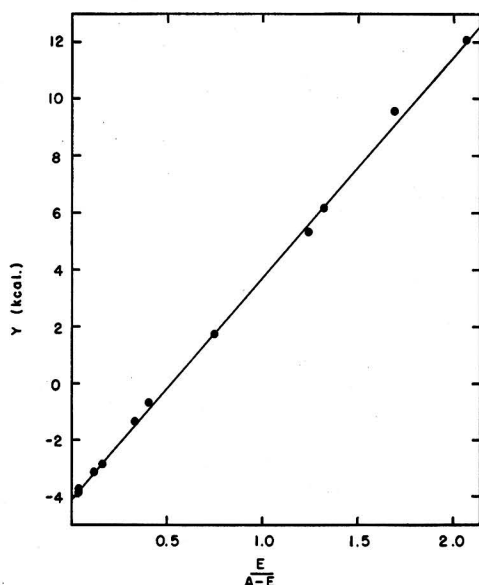


FIG. 1. Variation of the function of Y with the mole ratio of S^{2-} to HS^- .

straight line with slope equal to $\Delta H_{S^{2-}}^0$ and intercept equal to $\Delta H_{HS^-}^0$. The values of $\Delta H_{H_2S_{aq}}^0$, $\Delta H_{OH^-}^0$ and $\Delta H_{H_2O}^0$ (the standard heats of formation of H_2S_{aq} , OH^- , and H_2O) were obtained from Latimer (14).

The values obtained above for $\Delta H_{S^{2-}}^0$ and $\Delta H_{HS^-}^0$ along with K^I and K^{II} for H_2S allow a calculation of the remaining thermodynamic functions. We have taken $K^I = 1.02 \times 10^{-7}$ [Kubli's (3) value

corrected to 25°C] and $K^{II} = 1.3 \times 10^{-13}$ (from the extrapolated value of pK_u^{II} at zero ionic strength corrected to 25°C) (3, 7).

A summary of the results is presented in Table III. The limits of error are based on an estimated

TABLE III. Summary of results

	HS ⁻	S ²⁻
ΔF_{kcal}^0	3.00	20.6 ± 0.2
ΔH_{kcal}^0	-4.10 ± 0.08	7.8 ± 0.8
S_{su}^0	15.0 ± 0.4	-4 ± 3

uncertainty of 0.05 pK units in pK_u^{II} and 0.1 pK units in the extrapolated value, pK^{II} .

Using our value for $\Delta F_{S^{2-}}^0$, the potential of the sulfide-sulfur couple is:

$$S^{2-} = S + 2e^- \quad E^0 = 0.447 \pm 0.004 \text{ volt}$$

ACKNOWLEDGMENT

The authors wish to thank Dr. William L. Jolly for many helpful discussions in connection with this work.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Electrodes of Mixed Manganese Dioxide and Oxyhydroxide¹

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INTRODUCTION

To explain the decrease in open circuit electrode potential of electrolytic manganese dioxide electrodes during discharge and the slowness of their recovery from polarization, the assumption has been made that a solid solution of the reaction product and the manganese dioxide is formed (1). To test this assumption, electrode systems were constructed of mixtures of manganese dioxide and manganese oxyhydroxide, and the electrode potential was found to vary with the composition of the solid mixture.

EXPERIMENTAL

Preparation of the Manganese Oxides

A previously described (2) precipitated manganese dioxide preparation (II-MnO₂) was used for the electrode potential experiments. It was prepared by slow addition of a permanganate solution to a solution of manganese (II) sulfate and sulfuric acid. The precipitate, when washed and dried at 90°C, gave on analysis the manganese and available oxygen contents represented by the formula MnO_{1.967}. Available oxygen was determined by the arsenite method (3), and total manganese by potentiometric titration with permanganate in a pyrophosphate solution (4).

Manganese oxyhydroxide (MnOOH) was prepared by slow addition of ammonium persulfate solution to a solution containing manganese (II) sulfate, ammonium chloride, and enough ammonia to give a pH of about 8. The pH was maintained approximately constant during the reaction by addition of ammonia (5). The precipitate was dried at 90°C and analyzed as for the dioxide, the composition being MnO_{1.504}.

Mixed-Oxide Electrodes

A series of electrodes was prepared using the procedure previously described (2), but with mixtures

¹ Manuscript received October 27, 1952. Part of a thesis submitted by Richard S. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University.

² Present address: National Carbon Research Laboratories, Cleveland, Ohio.

of II-MnO₂ and oxyhydroxide. The two oxides in each mixture were weighed, mixed, and digested at room temperature for 24 hours with a solution of 1 mole/liter ammonia and 0.1 mole/liter ammonium chloride. This digestion has been shown to improve the constancy and reproducibility of electrodes (2). The solution was then removed by filtration and the oxide mixture washed with the electrolyte to be used. This was a solution of 2 moles/liter ammonium chloride and approximately 0.01 mole/liter ammonia, and had a pH of 7.5 as measured by a glass electrode and Beckman pH meter. Four electrodes were prepared from each oxide mixture. The compositions of the mixtures are given in Table I.

TABLE I. Potentials of electrodes of mixed manganese dioxide and manganese oxyhydroxide

Wt % of II-MnO ₂	Mole Ratio, R	log R	E, volts	E-0.073 log R, volts
100	14.0	1.146	0.500	0.416
90.0	5.0	0.702	0.462	0.411
69.6	1.75	0.243	0.442	0.424
50.2	0.83	-0.084	0.407	0.413
28.4	0.34	-0.472	0.382	0.416
10.5	0.101	-1.00	0.342	0.415
0	0		0.294	—

Electrode potential measurements were made occasionally over a period of 50 days. The potentials of the mixture electrodes (all but the first and last groups) decreased by an average of 60 millivolts during the first five days, which is considerably more than the usual decrease of similar electrodes made from manganese dioxide only (2). During the next three weeks the electrodes rich in dioxide decreased about 10 millivolts, while those rich in lower oxide were much more nearly constant, or increased. The change was much slower during the remainder of the 50-day period, and the values at the end of 50 days were accepted as a set of comparable values. The electrodes of the first group, containing none of the lower oxide, were constant after an initial decrease of 20 millivolts. The average deviation of the four electrodes in a group varied from 2 to 8 millivolts for the mixture electrodes and the pure oxyhydroxide group, which is more than for similar

electrodes of manganese dioxide only (2). At the end of 50 days, the pH of the combined electrolyte of each group of four cells was measured. All electrolytes were close to pH 7.1, and no corrections for pH differences were considered necessary.

It is worth noting that the electrodes made with the pure manganese oxyhydroxide were polarized so severely by small currents that it was necessary to use a vacuum-tube potentiometer for their measurement. This recalls the large polarization effect observed at the end of the discharge of electrolytic electrodes (1).

DISCUSSION

Table I gives the oxide compositions, in terms of weight per cent of the oxides actually used and as the calculated mole ratio, R , of dioxide to oxyhydroxide. In this calculation, II-MnO_2 was considered to be a mixture of the dioxide and the oxyhydroxide, in accordance with the analytical data. The corresponding values of the electrode potential, E , at 50 days are given in the fourth column. In the fifth are the values of E^0 in the equation

$$E = E^0 + 0.073 \log R \quad (I)$$

in which the coefficient 0.073 is empirical. The values of E^0 are in as good agreement as could be expected. It is not of first importance that the coefficient of $\log R$ is not 0.059, because R is a mole ratio rather

than an activity ratio. Also, there is some doubt as to the exact electrode reaction. However, the variation of E with R shows that the two solid phases are not independent of each other, but that the activity of at least one of them is affected by the presence of the other as would be expected if solid solutions are formed. Both E^0 and R may be expected to vary in different manganese dioxide preparations. Evaluation of the two should help to characterize a given preparation.

ACKNOWLEDGMENT

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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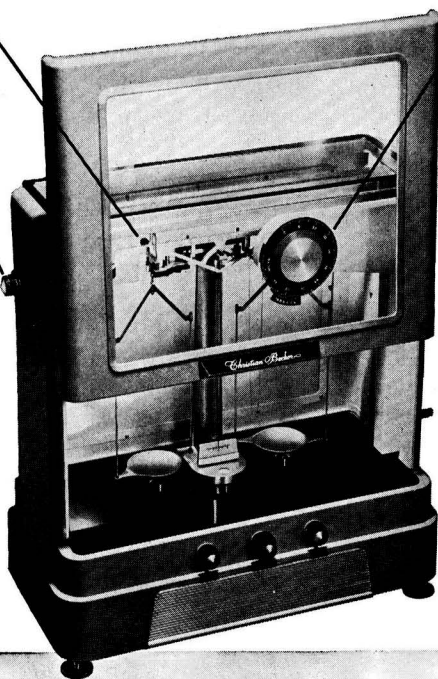
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The Electrochemical Society is an international organization of individuals and companies concerned with or interested in Electrochemistry and allied subjects.

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Battery	Electro-Organic
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Candidates for National Society Offices (1954-55)

Marvin J. Udy

Presidential Candidate

Marvin J. Udy, Consultant in metallurgical and electrochemical engineering, Niagara Falls, New York, is a native of Utah and a graduate of the University of Utah, class of 1915. He received the M. S. degree from the same school in 1916 and, in the two years following, was assistant research chemist at the



MARVIN J. UDY

U. S. Mining and Smelting Corporation in Utah.

Mr. Udy then came east to join the Hooker Electrochemical Company and later became chief chemist and research engineer of the Haynes Stellite Company. While there he developed a process for cadmium plating, the patents for which formed the basis of the Udy-lite Process Company, now of Detroit. Other connections of Mr. Udy include the Electrometallurgical Company of Niagara Falls, where he was employed for a period of eleven years, and the Swann Chemical Company of Alabama which he joined in 1931. Following this he became research and development engineer for Oldbury Electrochemical Company.

In 1937 Mr. Udy developed "Chrom-X" for the Chromium Mining and Smelting Company. "Chrom-X" is an exothermic ferrosilicon produced from low-grade chromite ores and has found a wide use in the steel industry. He at present enjoys a wide consulting practice in the metallurgical field and electric furnace smelting.

Mr. Udy was the recipient of the Schoellkopf Medal in 1948. He has been a member of The Electrochemical Society since 1919, serving for three years as Manager; he has also been vice-chairman and then chairman of the Niagara Falls Section. He was General Chairman for the 1950 convention at Buffalo.

Norman Hackerman

Vice-Presidential Candidate

Norman Hackerman was born in Baltimore, Maryland, in 1912. He received all of his college training, including graduate work, at Johns Hopkins University, receiving the Ph.D. degree in physical chemistry in 1935. Thereafter he was appointed assistant professor of chemistry at Loyola College in Baltimore, later serving as research chemist for the Colloid Corporation in that city. In 1941 he was appointed assistant professor of chemistry at Virginia Polytechnic Institute, which he left in 1944 to work on the Manhattan Project.

Dr. Hackerman joined the University of Texas staff in 1945; he is currently professor of chemistry, chairman of the department, and director of the Corrosion Research Laboratory. His research interests deal principally with the chemistry and physics of surfaces, especially as these phenomena apply to metal corrosion. Recently he and his students have published numerous articles on adsorption on metal surfaces and its influence on electrochemical properties and reactivity, and on the passivity of metals.

As a member of The Electrochemical Society, Dr. Hackerman served as chairman of the Corrosion Division in 1951, and has been Technical Editor of the *JOURNAL* since 1950. He belongs to the American Association for the Advancement of Science, and was the 1950 Chairman of the Gordon Corrosion Research Conference. He also holds membership in Phi Lambda Upsilon,



NORMAN HACKERMAN

Sigma Xi, The Faraday Society, the American Chemical Society, and the National Association of Corrosion Engineers, serving on the Board of Directors for the latter.

Frederick A. Lowenheim

Vice-Presidential Candidate

Frederick A. Lowenheim was born in 1909 in New Rochelle, New York. After the conventional schooling there, he attended Columbia University, where he received his B.A. degree in 1930 and the Ph.D. degree in chemistry in 1934. For his thesis he worked in the field of transference numbers in the nonaqueous solvent sulfuric acid, as a student of Professor L. P. Hammett.

After a short time in another position, Dr. Lowenheim came to Metal and Thermit Corporation in 1936; he is now supervisor of Electrochemical Research at the company's Woodbridge, New Jersey, Laboratories. His work has been of varied nature, including different phases of inorganic technology. In recent years, he has tended to concentrate in the electrochemical field with particular emphasis on electro-deposition, especially of tin and its alloys. He has contributed papers on this and related subjects to the *TRANSACTIONS OF THE ELECTROCHEMICAL SOCIETY* as well as to many other



FREDERICK A. LOWENHEIM

publications, and he holds several patents in this field. During the war, he was particularly active in the strip steel electroplating program. For the past three years, he has conducted a series of lectures at Stevens Institute of Technology on advanced inorganic chemistry.

Dr. Lowenheim's activities in The Electrochemical Society have included the chairmanship of the Electrodeposition Division and of the New York Metropolitan Section; he has more recently served the New York Section as Secretary-Treasurer. He is particularly interested in the affairs of the local sections, being at present Chairman of the Local Section Advisory Committee; and he has served as Finance Chairman for three national conventions, two in New York and one in Wrightsville Beach. He is a member of the Editorial Advisory Board and has contributed chapters to the forthcoming Electrochemical Society Monograph on "Modern Electroplating."



JOHN R. MUSGRAVE

John R. Musgrave
Vice-Presidential Candidate

John R. Musgrave, Chief Physicist in the Eagle-Picher Research Laboratories at Joplin, Missouri, was born at Reading, Pennsylvania, in 1906. He received his degree in chemical engineering at Lafayette College in 1927. Following a period of industrial research, he entered the graduate school of the University of Toronto. There he received the Ph.D. degree, majoring in physical chemistry, in 1933. Shortly after the completion of his graduate work, he became affiliated with the Eagle-Picher Research Laboratories, where he is, at present, in charge of the Physical-Chemical Section of the Laboratories.

Dr. Musgrave's research activities cover work on thermal insulation, storage batteries, paint, corrosion, instrumentation, diatomaceous earth, and rare metals. He has been active in the development of high-purity germanium for semiconductor work, as well as gallium. He holds several patents and is the author or co-author of technical papers on storage battery technology, particle-size determination (in the sub-sieve range), germanium, and gallium.

Dr. Musgrave joined The Electrochemical Society in 1941 and has been particularly active in the Battery and Electronics Divisions. He has been secretary-treasurer and chairman of the Electronics Division and has participated in the development of the rare metals and semiconductor symposia. He is presently a member of the Acheson Award Committee as well as several other Society committees. He is also a member of a number of other scientific organizations.

Corrosion Division Essay Winners

The first prize of one hundred dollars for the best essay on the topic "Contributions of Electrochemistry to Science" is to be shared equally by Ahmad Geneidy of West Virginia University and Alvin P. Ginsberg of New York University. Each will receive also a one-year membership in the Society. The second prize of fifty dollars has been awarded to Robert S. Johnson of Monmouth College, Monmouth, Illinois. He, too, will receive a one-year membership in the Society. The following contestants were given honorable mention and a year's subscription to the *JOURNAL*: Eugene Ashby (address not furnished); Robert Auerbach, New York University; Herbert L. Bullard, John B. Pierson, Richard Prouty, and Elizabeth Holmes, all of Alabama Polytechnic Institute; Miss Jariwala L. Jayshri of St. Xavier's College, India; and Dorothy Bump (now Mrs. Clinton Ryno), Roger Ray, Elwood Richard, and Warren Trask all of Monmouth College.

These young people are all to be congratulated upon the well-written and thoughtful papers which they submitted. It is to be hoped that what they learned about electrochemistry has stimulated an interest in this subject and in science generally. The Society is gratified at the encouragement to student interest in the prize essay contest shown by the institutions with which these contestants were connected. The Corrosion Division, in sponsoring a prize essay contest, is making an important contribution toward publicizing in the colleges and universities the nature and accomplishments of electrochemistry and the existence of this Society.

Electronics—Semiconductor Symposium Planned for Chicago

The Semiconductor group of the Electronics Division is planning a symposium for the Chicago Meeting, to be held May 2-6, 1954. This symposium will feature intermetallic compound semiconductors such as the antimonides, arsenides, and phosphides. In addition, sessions are planned for germanium, silicon, and other semiconductors.

Papers will be considered on new and old semiconductors, their electrical, chemical, and metallurgical properties, and preparation and fabrication meth-

ods; closely associated geometrical and electrical requirements on imperfections in semiconductors, and mechanical and chemical combinations of semiconductors with other materials to achieve a particular solid-state electrical device; techniques of producing conducting films and compositions, and devices made from them, as well as analytical studies of effects of environmental conditions on surface and bulk properties and structure of semiconductors and semiconductor devices; and closely related subjects.

Five copies of manuscripts or abstracts (not to exceed 75 words in length) must be received at Society headquarters, 216 West 102nd Street, New York 25, N. Y., not later than January 15, 1954. The title of the paper should also be sent to the Chairman of the symposium, A. E. Middleton, Battelle Memorial Institute, Columbus 1, Ohio.

A second "extended abstract" of about 1000 words must be submitted not later than February 1, 1954 to A. E. Middleton. This extended abstract is "printed, but not published" in a booklet which will be available, at cost, before and during the meeting. Abstracts of papers (luminescence, screen applications, etc.) presented in other groups of the Electronics Division will also appear in this booklet.

Bell Labs Develops Important New Diode

A new electronic device which may result in revolutionary advances in telephone switching systems and in many kinds of computers has been created by Bell Telephone Laboratories, research and development organization of the Bell System.

Described as a silicon alloy junction diode, it serves as the electronic equivalent of a tiny one-way switch. Thus it acts as a rectifier. Also, it is capable of operating thousands of times faster than its mechanical counterparts. Switches of this type can perform as deft fingers operating the telephone dial system—or enabling mechanical computers to make complex calculations in a fraction of a second.

A diode may be compared to a pipe with a check valve which allows water to flow in one direction but blocks it from flowing in the opposite direction. The back leakage, which is never completely prevented, is smaller than in any previous diode—and the leakage currents of vacuum-tube diodes may be a thousand times greater. The new diode

also contrasts sharply with the two-element vacuum tube in that it requires no filament or vacuum. It has an encased element no larger than a match head, and is an accomplishment growing out of transistor research and development. Its lifespan should be almost unlimited.

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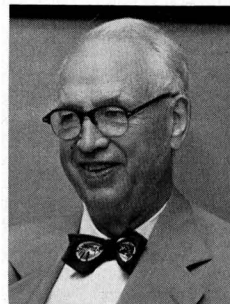
Dedication of a new \$2,600,000 research center at The Dow Chemical Company's Texas Division in honor of Dr. William Reed Veazey, recently retired Dow director and research consultant, will take place in October.

In its 69,000 ft² of space, the research center will house the Texas Division's organic, chemical engineering, and electrochemical research, as well as the analytical laboratory, and will also include research administrative offices, a patent office, and a library.

Dr. Veazey began his association with Dow in 1915, when he undertook special research work in magnesium. At the time he was an assistant professor at the Case School of Applied Science, now Case Institute of Technology, in Cleveland. In 1916 he headed a developmental group which

succeeded in producing the first pound of magnesium metal ever made in the States.

Dr. Veazey remained on the Case staff until 1936, meanwhile continuing special Dow work; that year he resigned



from Case to join Dow permanently in Midland. He served successively as coordinator of research, patent and product development, head of the Executive Research Committee, and as a research consultant.

He is a past president of The Electrochemical Society and has been a member of the American Chemical Society and the American Institute of Chemical Engineers for many years. At the time

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of his retirement, Dr. Veazey was a director and vice-president of Dowell Incorporated, a Dow subsidiary, and a director of Dow Corning Corporation, an associated company.

New Development by Lindberg Engineering

Carbon and sulphur contents of ferrous alloys can be determined in a single operation with procedure introduced by the Laboratory Division of Lindberg Engineering Company, Chicago, Illinois. The procedure uses the Lindberg High Frequency Combustion Unit to heat specimens by inductive heating to temperatures above 3000°F. Heat is generated in the sample only.

Lithium Corp. Liquidates Subsidiary

K. M. Leute, president of Lithium Corporation of America, Inc., Minneapolis, Minn., has announced that, effective July 1, 1953, the company has liquidated its wholly owned subsidiary, Metalloy Corporation. Metalloy previously has operated as the chemical and sales division of the parent company. Hereafter, all business will be conducted under the name of Lithium Corporation of America, Inc.

PERSONALS

JOHN J. STOBIE, Apex Smelting Company, Chicago, Ill., has been appointed sales engineer of the company's West Coast plant and will be located at Apex Smelting Company, Long Beach, Calif.

WALTER BECK has joined the Department of Materials Engineering, Syracuse University, East Syracuse, New York. Dr. Beck formerly resided in New York City.

ROBERT L. CRONE is now associated with the Hughes Aircraft Company of Culver City, California, as a member of the technical staff. Mr. Crone was formerly with Radio Corporation of America, Victor Division.

RALPH M. HUNTER, prominent in the nation's electrochemical industry, has been advanced to the position of staff coordinator of all electrochemical activities for the Dow Chemical Company, according to a recent announcement. In his new capacity Dr. Hunter will coordinate electrochemical operations on a company-wide basis and facilitate the exchange of research and devel-

opment information. He will, however, retain active charge of the Midland Electrochemical Laboratory.

CLIFFORD A. HAMPFEL, chemical engineering consultant, of Homewood, Illinois, has been elected president of the Chicago Technical Council, a federation of scientific, engineering, and technological societies. Mr. Hampfel is editor-in-chief of the *Encyclopedia of Chemical Reactions*, and is currently engaged in editing a forthcoming *Handbook of Rare Metals*.

RUSSELL B. SNYDER has recently been named second vice-president of The Rauland Corporation, Chicago, Illinois. He was formerly Chief Chemist of the company.

D. GARDNER FOULKE, formerly chief chemist at the Hanson-Van Winkle-Munning Company, Matawan, New Jersey, has been appointed manager of electrochemical development of the company.

I. MELVILLE STEIN, formerly executive vice-president of Leeds and Northrup Company, Philadelphia, Pa., has been elected president of the company. Mr. Stein joined Leeds and Northrup in 1919. During World War I, he had been personal assistant to Thomas A. Edison when the inventor was chairman of the Naval Advisory Board and was cited for his work throughout World War II. In 1928, he was appointed director of research at Leeds and Northrup, in 1944 vice-president, and in 1951 executive vice-president.

ROBERT M. PARKE has been promoted to manager of the materials and processes section of the Metallurgy Research Department, General Electric Research Laboratory, Schenectady, New York.

EDWARD B. SANIGAR

Edward B. Sanigar of the Naval Radiological Defense Laboratory, San Francisco, died on July 28, of a heart ailment.

Dr. Sanigar joined The Electrochemical Society in 1929 and was one of its active workers. Among his activities in the Society were service on the Publication Committee, Vice-Chairman of the San Francisco Section, and Chairman of the same Section.

Dr. Sanigar received the B.Sc. and M.Sc. degrees from Sheffield University and he studied at Columbia University on the Edward Weston Fellowship. He

was investigator for the British Government Electrodeposition Committee and the British Non-Ferrous Metals Research Association from 1926-29. For the following two years he was research chemist at Leeds and Northrup Company in Philadelphia. From 1933-35 he served as research chemist and investigator in cancer research at Pennsylvania Medical School. He joined the staff of the Biochemical Research Foundation, Franklin Institute, as a research physical chemist in 1935, becoming head of the physical chemistry department in 1941. In 1947 Dr. Sanigar became associated with the radiation laboratory of the San Francisco Naval Shipyard as a physical chemist and the following year was appointed Assistant Scientific Director of the Naval Radiological Defense Laboratory, continuing in this capacity until the time of his death.

LETTER TO THE EDITOR

Oxidation of Metals at High Temperatures

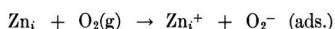
Dear Sir:

The recently published paper with this title¹ included a suggested mechanism for oxidation of Ti and Zr that is probably not valid. It was stated that the large negative entropy of activation ΔS^* for the parabolic oxidation rates of these metals might be due to diffusion via anionic vacancies. It should have been evident, however, that such anionic diffusion cannot yield a large negative ΔS^* , since the concentration of oxide-ion vacancies would be highest at the metal-to-oxide interface and close to zero at the oxide-oxygen interface. Thus, the formation of anion vacancies in films of ZrO₂ and TiO₂ would not be associated with the loss of freedom of gaseous oxygen that can lead to large negative ΔS^* . On the other hand, inward migration of interstitial oxygen or of oxygen along grain boundaries would lead to negative ΔS^* values. The higher temperature oxidation of Zr (500°-900°C) with $\Delta H^* = 32.0$ kcal and $\Delta S^* = -7.1$ cal deg⁻¹ may, however, represent anionic vacancy migration.

In view of the evidence available at present, it now seems most likely that the oxidations of Zn, Al, Ti, and Zr, at temperatures below 500°C, all proceed by migration of interstitial

1. W. J. MOORE, *J. Electrochem. Soc.*, **100**, 302 (1953).

cations. The large negative ΔS^* then arises because the cations are formed from interstitial atoms by some reaction such as the following:



This reaction would lead to the loss of the entropy of oxygen (S_1), the gain in entropy by formation of a tightly adsorbed $\text{O}_2^- (S_2)$, and some gain in entropy due to replacement of Zn_i by $\text{Zn}_i^+ (S_3)$. Thus, with reasonable estimates of the entropies involved,

$$-\Delta S = S_1 - S_2 - S_3$$

$$= 50 - 10 - 10 = -30 \text{ cal deg}^{-1}$$

The experimental ΔS^* values range from -23 to -29 , so that a reaction of the type proposed can readily account for the observations. It has already been shown how this mechanism serves to explain the experimental values of the activation energies.²

The electric field caused by the surface oxide ions may also affect the migration rates of the interstitial cations, as has been emphasized by Cabrera and Mott³ and by Engell and

2. W. J. MOORE, *J. Chem. Phys.* **20**, 764 (1952).

3. N. CABRERA AND N. F. MOTT, *Rep. Prog. Phys.*, **12**, 163 (1949).

Haufler.⁴ The latter authors are probably correct in their analysis of the pressure dependence of zinc oxidation⁵ as evidence for the electric field effect.

It should now be evident that, for both n - and p -type oxides, large negative ΔS^* in parabolic rate constants can be explained in terms of the loss of freedom of the attacking gas in the step leading to formation of the migrating defects.

W. J. MOORE

Indiana University
Bloomington, Indiana

4. H. J. ENGELL AND K. HAUFFE, *Metal*, **6**, 285 (1952).

5. W. J. MOORE AND J. K. LEE, *Trans. Faraday Soc.*, **47**, 501 (1951).

BOOK REVIEWS

FERROELECTRICITY by E. T. Jaynes.

Published by Princeton University Press, Princeton, N. J., 1953. 146 pages, \$2.00.

This short book does not attempt to cover the entire subject. It is primarily a rather well done critical review of the theories of ferroelectricity, aimed at

guiding the research worker through a literature extraordinarily full of errors, misunderstandings, and conflicting points of view. Secondly, the author gives in detail a number of his own new theoretical results. The best thing about the book is that one comes away with the correct impression that most of the questions are still open. On the other hand there is no attempt to give the reader general background in the subject, and only a sketchy discussion of the experimental work.

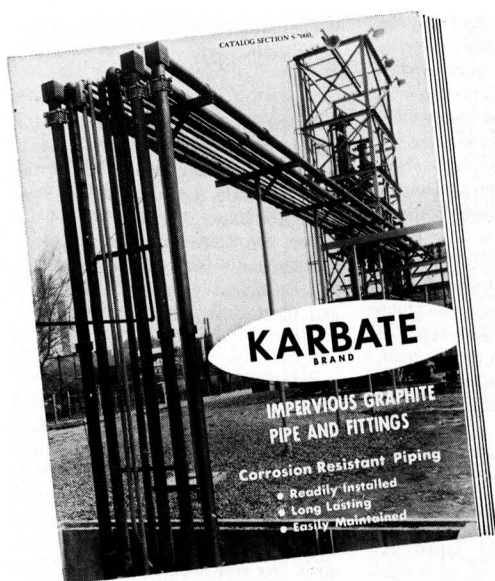
This book will be valuable to the research worker in the field of ferroelectricity, but of little use to the more general reader.

P. W. ANDERSON

QUANTITATIVE ANALYSIS by Harvey Diehl and G. Frederick Smith, 539 pages. John Wiley & Sons, Inc., New York, and Chapman & Hall, Limited, London, 1952, \$5.

This is an excellent elementary textbook on quantitative analysis, designed for use in second-year college work. Its 19 chapters cover all of the customary theory and practice of chemical analysis in a well-organized, well-illustrated, and clearly presented man-

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ner. The book should be most welcome to teachers, for the subject has been so skillfully handled in most instances that very little amplification on the part of the instructor is necessary. Students will also find it attractive because the style is such as to make the context easily understood:

The book has been written by two of this country's most eminent analytical chemists. Since their efforts have been largely directed toward the development of useful methods of chemical analysis, it is natural that the new textbook reflects the approach of the practicing analytical chemist. Detailed instruction in the important manipulations of analytical chemistry has been stressed in place of the usual, somewhat excessive, emphasis on theory. This is not to imply that theory has been ignored. In fact, the book places about equal emphasis on theory and practice.

Because of the enthusiasm for analytical chemistry reflected in the writing and because every attempt has been made to use up-to-date knowledge and examples, the textbook should stimulate interest in analytical chemistry as a career.

C. L. LUKE

ELEKTROLYTISCHES HÄRTEN (Electrolytic Hardening) by I. S. Jasnogorodski. Translated from the Russian (1949) by Fr. Krantz. Published by Verlag Technik GmbH., Berlin NW7, 1951. 119 pages, approximately \$4.35, cloth bound.

The subtitle of this book is "The Heating of Metals and Alloys in Electrolytes." There is a six-page editorial preface explaining the importance of the new method compared to high-frequency induction heating, and mentioning that Jasnogorodski received the Stalin prize in 1947 for the discovery.

Briefly, Jasnogorodski's process consists in treating the surface to be heated as cathode in 5 to 10 per cent sodium carbonate solution at 50° to 70°C and about 200 volts or more of direct current, giving a current density of about 30 amp/in.² Under these conditions, the surface is heated to a very high temperature in from 5 to 10 seconds, and may even be melted. A peculiar light is observed at the cathode, and the author presumes that the heat effect is due to the formation and recombination of hydrogen atoms.

The first chapter describes the work done to investigate the effect of different variables on the process, and the results

with a number of different electrolytes. The second chapter describes the process decided upon for commercial work, and some of the equipment used and results obtained. The third and fourth chapters relate largely to a number of automatic and special purpose machines developed by the author for treating various types of parts, welding, sintering, hot forging, and so on.

On the face of it, the book appears to describe a remarkable new process which may prove to be of widespread interest. The principal advantages claimed are high heating velocity, control of area and depth of hardening, avoidance of oxidation, and adaptability to use in automatic machines.

The book seems well written and well illustrated, with 79 figures including line drawings, photographs, and curves. The new development is described entirely without benefit of bibliography, and one wonders if there is no previous similar work or prior art. The author indicates that his investigations began in 1937.

G. DUBPERNELL

LITERATURE FROM INDUSTRY

COLLOIDAL GRAPHITE. New six-page, two-color bulletin on "Colloidal Graphite for Surface Coatings and Impregnation" is now available. Electric furnace graphite of high purity, when rendered colloidal and dispersed in a suitable carrier, finds new uses as a dry-film lubricant—surface coating for many mechanical devices—and as impregnating medium for such materials as porous minerals, cloth, asbestos, and paper. Acheson Colloids Co. P-157

PUMP APPLICATION GUIDE. A new type of reference chart on small pump applications lists the various types of pumps, services for which each is built, and the performance and special features of each. Tuthill Pump Co. P-158

DIMENSIONAL DATA SHEETS. A new series of dimensional data sheets on a line of valves for fluid control has just been released, giving complete valve dimensions. They should prove extremely valuable in planning or designing new equipment in instrumentation or industrial fields. Hoke, Inc. P-159

DIFFERENTIAL VOLTAGE INDICATOR. Bulletin describes a new indicator.

designed to measure differential voltage, as well as amperage, speed, pressure, and other quantities which can be converted to voltage. The device features a self-balancing circuit which possesses a high degree of stability and freedom from drift. Can be used with standard accessories, such as a recorder, indicating instrument, or alarm relay. General Electric Co. P-160

POWER SUPPLIES. Twenty-page catalogue and new condensed brochure have just been released describing Voltage Regulated Power Supplies. Of interest to all users of electrical and electronic equipment. Kepeco Laboratories, Inc. P-161

GAGES AND VALVES. New folder describes line of liquid level gages and valves, water columns, gage illuminators, etc. Features include safety, readability, and pressure. Jerguson Gage & Valve Co. P-162

YARDNEY SILVERCELS. Brochure and technical data sheets announce several new high-capacity models of silver-zinc alkaline cells which feature unusually high discharge currents and are rated at 100 amp-hr. Up to six times lighter and five times smaller than ordinary storage cells of comparable capacity; spillproof and highly efficient; free from corrosive fumes, vapors, spray, and gassing; high discharge rates; and flat output voltage characteristics. Yardney Electric Corp. P-163

NEW CLAD METALS. New pamphlet describes nine new developments in the field of clad metals. Detailed information given on the cuprum anode, the ferrolum anode, ferrolum lead clad steel immersion heater, the Knapp lead-plate heater, the Universal pipe supporter, the automatic lead cladding machine, Knapp Raysist compounds, lead-lube, and the Guidler. Knapp Mills Inc. P-164

PLASTIC COATING AND COMPOUND. Two new leaflets on plastic coating, and cleaning and phosphate coating have been published. The former describes the use and application of a new vinyl-type coating for paint spray booths. The coating is easily peeled off, taking with it all paint overspray, to give quick, low cost maintenance. The latter leaflet describes a compound use for cleaning and imparting a fine-grained phosphate coating to steel parts to provide a good paint bond. Detrex Corp. P-165

NEW PRODUCTS

HIGH PRESSURE FILTERS. High pressure liquid and gas filters have been added to the line. Standard units are available for operating pressures up to 1000 psi; filters for even higher pressures also available. Construction is all welded steel. Cuno Engineering Corp. N-28

METAL CLEANER. New metal cleaner, Detrex 63, specially formulated for use in the vitreous enameling industry, has been developed. Described as a medium-high alkaline compound containing very high wetting and penetrating properties. Exceptional ability is claimed for emulsifying large quantities of mineral oils and greases and for keeping them in a state of suspension. Detrex Corp. N-29

NEW "B" TYPE BATTERY. Smallest alkaline-type "B" battery designed for use in current personal portable radios has been announced. This midget 45-volt "B" battery (VSO86) weighs approximately 3 oz. and is $3\frac{3}{16}$ in. long, $1\frac{1}{16}$ in. wide, and $1\frac{1}{16}$ in. deep. The small size and excellent performance stem principally from its alkaline-cell construction which permits more efficient utilization of the battery cell's active materials. RCA Victor Division, Radio Corporation of America. N-30

AUTOMATIC RECLOSING RELAY. An automatic reclosing relay (RC) with a built-in instantaneous trip lockout feature is now available. Applicable to all types of circuit breaker control schemes. Adjustable reclosing time sequences of 60, 90, 180, or 360 seconds are provided by a 600-rpm synchronous motor with a gear train of adjustable ratio. May also be obtained with an adjustable integrating lockout device which limits successive circuit breaker reclosures to a safe value. Westinghouse Electric Corp. N-31

ELECTRO POLARIZER AND PORTABLE GALVANOMETER. Chemical analysis of plating solutions now can be analyzed with a great degree of accuracy and speed by means of an electro polarizer and a portable galvanometer. The new Patwin electro polarizer utilizes the polarographic method of analysis and can be used to analyze most plating solutions, including copper cyanide, zinc cyanide, cadmium, brass, and nickel. The G-E galvanometer measures

the low values of current or voltage. Its high sensitivity is made possible by alnico magnets, which provide a field of more than twice the strength obtainable with chrome-steel magnets. General Electric Co. N-32

STABILIZED CRYSTAL. A new stabilized crystal, the JK G-12, specially designed to handle applications in the "difficult" 500 to 1500-kc range, has just been introduced. The unit provides ultra-stable frequency control for applications such as frequency standards, timing and counting circuits, broadcast equipment, and frequency monitors. Use of the evacuated glass envelope assures freedom from contamination, and greater shock resistance. James Knights Co. N-33

To receive further information on any New Product or Literature from Industry listed above, send inquiry, with key number, to JOURNAL of The Electrochemical Society, 216 West 102nd Street, New York 25, N. Y.

Please print your name and address plainly.

RECENT PATENTS

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

May 5, 1953

- Kendall, T. L., and Gentry, D. P., 2,637,209, Electrolyte Level Indicator
 Udy, M. J., 2,637,648, Production of Ferrosilicon
 McKay, R. J., 2,637,686, Process of Producing Drawn Articles
 Portzer, L. B., and Leitenberger, W. C., 2,637,687, Electrodeposition of Nickel
 Ryan, E. J., 2,637,688, Method of Polymerizing Oxygen
 Myers, R. R., Jr., 2,637,689, Device for Making Curved Electroplate Shells
 Coleman, J. J., and Wilke, M. E., 2,637,756, Deferred Action Battery
 Wilke, M. E., 2,637,757, Deferred Action Battery
 Shannon, J. K., 2,637,758, Storage Battery
 Shannon, J. K., 2,637,759, Storage Battery Cell Cover and Construction
 Boyer, J. L., and Albert, W. S., 2,637,827, Alkali-Metal Rectifier
 Sharkey, A. J., 2,637,830, Treatment of Electric Lamp Envelopes

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- Nelson, H. F., 2,637,760, Storage Battery Testing and Filling Apparatus
 Kendall, T. L., Bodenhafer, C. B. and Plummer, R. I., 2,637,836, Method for Charging Storage Batteries

May 12, 1953

- Nachtman, J. S., 2,637,896, Manganese Alloy Coating on Ferrous Base and Method of Preparation
 Schoch, E. P., 2,638,443, Method and Apparatus for Glow Discharge Treatment of Gases
 Ruben, S., 2,638,489, Primary Cell
 Snyder, A. H., 2,638,490, Storage Battery and Lift Device

May 19, 1953

- Chester, A. E., 2,639,264, Vitreous Enameling Processes and Products
 Simeox, H. J., 2,639,265, Anodes for Cathode Protection of Metal Structures
 Wills, W. P., 2,639,305, Annular Thermocouple
 Fischbach, A., 2,639,306, Pile Battery Fabrication
 Lafferty, J. M., 2,639,399, Electron Emitter

May 26, 1953

- Jacobs, H. and Hees, G., 2,639,996, Filamentary Cathode
 Pollard, C. E., Jr., 2,640,020, Formation of a Surface Easily Wettable by Mercury
 Passal, F., 2,640,021, Composition, Bath, and Process for Chromium Plating
 Stareck, J. E., 2,640,022, Composition, Bath, and Process for Chromium Plating
 Cier, H. E., 2,640,023, Photochemical Production of Branched Paraffinic Hydro-Carbons
 Palmateer, R. E., 2,640,024, Electrophoretic Borating of Copper Wire
 Lazaro, A. M., 2,640,025, Electroplating Barrel
 Whittington, P. E., 2,640,026, Electric Filtering Apparatus
 Gilbert, R. W., 2,640,089, Thermocouple Cold-End Compensator
 Pucher, L. E., and Cunningham, W. A., 2,640,090, Battery
 Pucher, L. E., and Cunningham, W. A., 2,640,091, Battery
 Nevin, S., 2,640,169, Heated Cathode Electron Multiplier

June 2, 1953

- Hesch, F. H., 2,640,806, Process for Polishing Aluminum
 Skinner, R. E., and McIntyre, G. H.,

- 2,640,859, Apparatus for Producing Porcelain Enamel
 Herres, S. A., 2,640,860, Apparatus for Melting Titanium to Form Ingots
 Kremers, H. C., 2,640,861, Resistance Furnace
 Chubb, M. F., 2,640,862, Battery Pigment
 Ellis, G. B., 2,640,863, Deferred Action Type Battery
 Fishbach, A., and Hochberg, F., 2,640,864, Preparation of Porous Zinc Electrodes
 Brennan, J. B., 2,640,865, Storage Battery
 Swanson, H. T., 2,640,952, Hydrogen Pressure Control for Hydrogen Filled Discharge Tubes

June 9, 1953

- Mohling, G., and Dyrkacz, W. W., 2,641,540, Ferrous Base Chromium-Nickel-Titanium Alloy
 Litton, C. V., 2,641,555, Nonemissive Electrode and Method of Making
 Sachs, C. C., and Bond, J., 2,641,576, Photopolymerization Process and Compositions
 Greene, A. E., 2,641,621, Electric Induction Furnace
 Higgins, W. F., and Wilkinson, R. G., 2,641,622, Electric Primary Cell
 Winckler, G. A. F., and Reinhardt, O. K., 2,641,623, Primary Battery Cell
 Winckler, G. A. F., and Reinhardt, O. K., 2,641,624, Cell
 Elmer, W. B., 2,641,625, Battery Container
 Parrish, N. C., 2,641,672, Electrical Conductor

June 16, 1953

- Wallace, de Yarman, and Mansell, L. R., 2,642,368, Coating Metal Articles by Dipping in Bath of Dissimilar Molten Metal
 Garofano, J., 2,642,390, Process of Ornamentation of Articles Made of Plastics
 Wellman, W. C., 2,642,391, Anodic Rod Holder
 Sommers, C. J., 2,642,392, Electroplating Apparatus
 Dodson, J. I., 2,642,468, Thermocouple Mounting for Use in Molten Steel
 Gary, W. W., Jr., 2,642,469, Alkaline Battery
 Reinhardt, O. K., and Welsh, J. Y., 2,642,470, Dry Cell
 Reinhardt, O. K., and Stapleton, T. C., 2,642,471, Dry Cell
 Shave, R. E. J., 2,642,480, Indicator for Eutectic Coolers
 Urbach, F., 2,642,538, Thermal Radiography Using Phosphors

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June 23, 1953

- Zimmerman, H. M., 2,642,628, Method of Forming a Wet Cathode Portion
 Ahrens, G. W., 2,642,654, Electrodeposited Composite Article and Method of Making the Same
 Savidge, L. N., and Thomas, R., 2,643,197, Fluorescent Alkoxy Benzoyl Derivatives of 4,4' Diamino Stilbene-2,2' Disulfonic Acid and Detergent Compositions Containing Same
 Savidge, L. N., and Thomas, R., 2,643,198, Fluorescent Compound and Methods of Imparting Fluorescent Effects to Materials
 Brenner, A., Couch, D. E., and Williams, E. K., 2,643,221, Electrodeposition of Phosphorus-Nickel and Phosphorus-Cobalt Alloys

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