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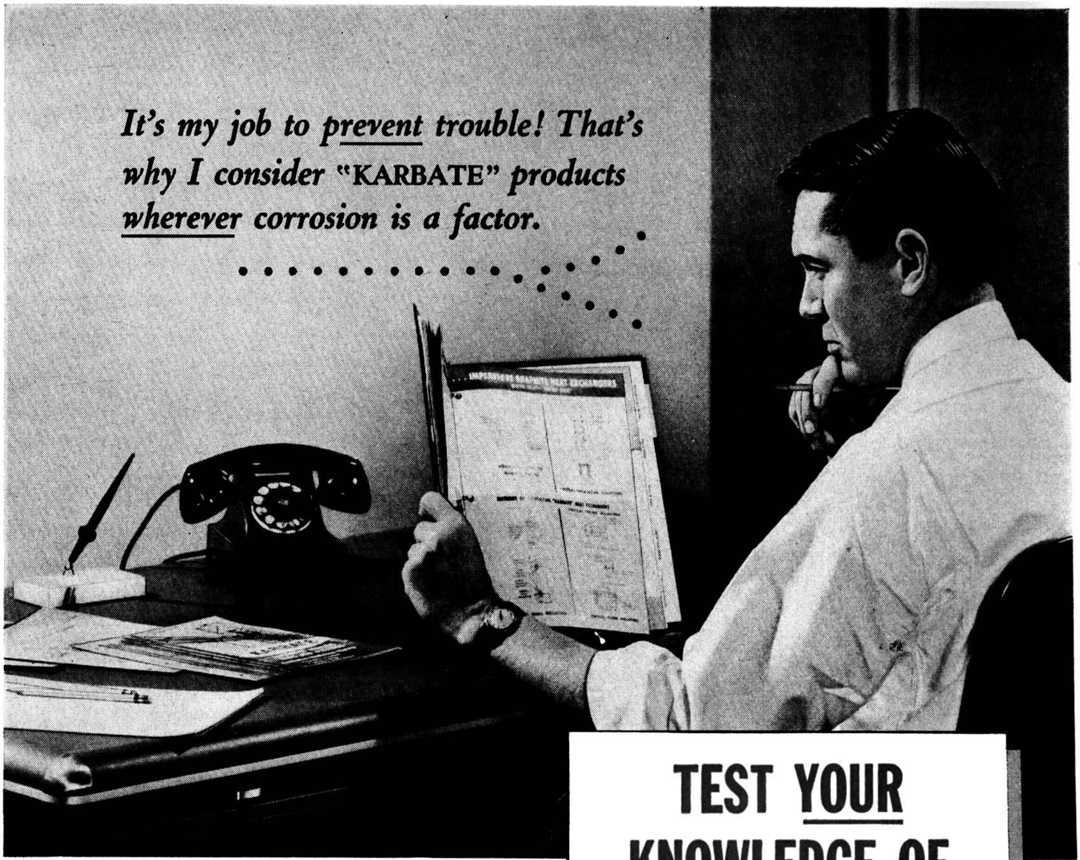

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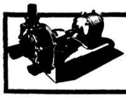
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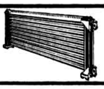
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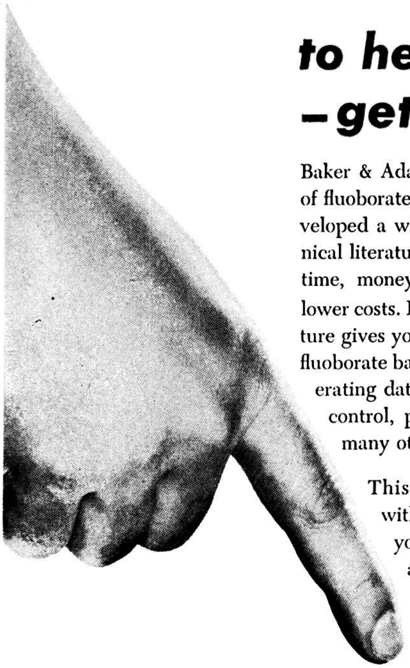

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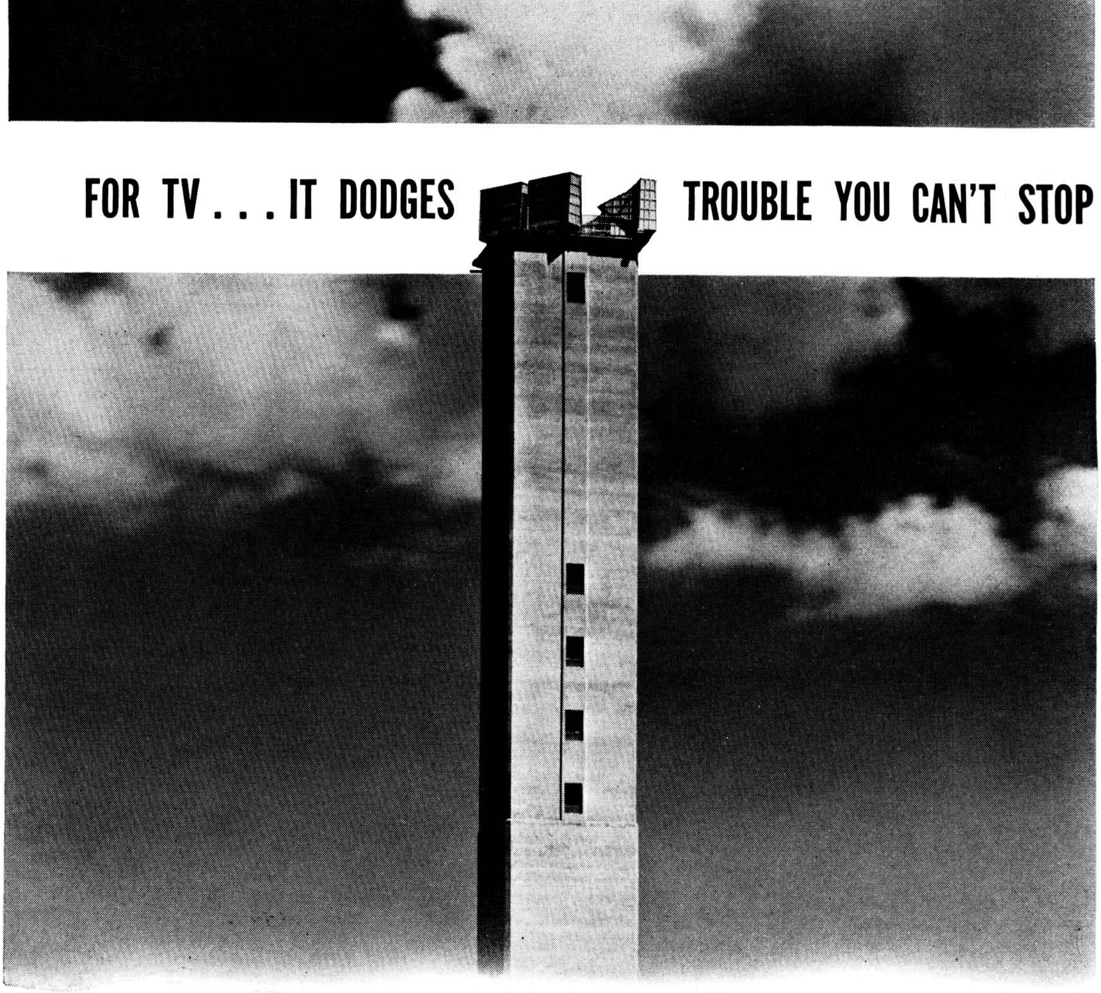

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Self-Sufficiency for National Security

THE WESTERN HEMISPHERE can be made self-sufficient in the production of the necessary critical materials for our peacetime economy and for the conduct of all-out war. This is the conclusion of the Minerals, Materials, and Fuels Subcommittee of the Senate Committee on Interior and Insular Affairs after extensive hearings. Among the recommendations of this group, headed by Senator Malone, is that an annual appropriation of fifty million dollars be made to establish and operate a comprehensive five-year program of laboratory, pilot-plant, and exploratory research into improved methods of beneficiation of critical materials and the study of substitutes, including synthetics and replacements. This is a most constructive proposal and it is to be hoped that it will be implemented by Congressional action.

The scarcity of some 77 critical and strategic materials on which national survival in time of war would depend is to some extent the result of a desire to conserve our own natural resources. Conservation is laudable insofar as it leads to economical use, but it lends little incentive to exploration or process development for the extraction of essential materials from these resources. Another impulse contributing to our uncomfortable critical materials situation is the widespread desire to promote world trade as a means of achieving world peace. National security, however, dictates that we should not depend on areas for the production of essential raw materials or sea lanes for their transit that are vulnerable to enemy attack. This means that the Western Hemisphere must be self-sufficient and that whatever measures are necessary to achieve this goal must be undertaken.

One of the most fruitful means for the attainment of materials self-sufficiency is through research—exploratory research toward the discovery and beneficiation of critical materials and particularly research of the most fundamental kind for the discovery of new knowledge. There is little doubt that intensive mineral exploration will reveal unsuspected reserves of essential materials and that electrochemical and metallurgical methods can be devised for the practical extraction of many critical metals from complex and low-grade ores.

The large programs of product research that have become a spectacular feature of American industry and that have contributed so much to modern life have not revealed much new scientific knowledge of the basic kind. Yet it is only by research directed toward the discovery of new scientific facts that the background can be prepared for any substantial progress toward the synthesis of essential raw materials or the development of any really new or improved compositions of matter that can be substituted for critical materials. That basic research does lead to such ends can be illustrated by the synthesis of quartz, the discovery of the transistor, and the development of a practical means for producing metals in which impurities are controlled at levels below one part in a billion.

Synthetic quartz can make importation of this essential material unnecessary, if desired, even though Brazil is the source of the natural product. The transistor not only makes possible a vast expansion of electronic technology but encourages the miniaturization of electronic devices with substantial economies in the use of materials and power. Finally, ultrapurification promises to improve the properties and performance of many abundant metals to such a degree as to encourage their substitution for some of the more critical metals. Many other examples could be cited of the practical value of basic research.

It is apparent that the proposed governmental appropriation for the support of materials research is decidedly in the national interest. Beyond this, definite measures should be taken to encourage the chemical and metals industries to devote an appreciable effort to fundamental research. Congressional study should determine whether this can be accomplished best by selective tariffs, tax law changes, or by other means. The expenditure by American industry of a hundred million dollars a year for really basic research would assure materials self-sufficiency, an expanding peacetime economy, and national security!

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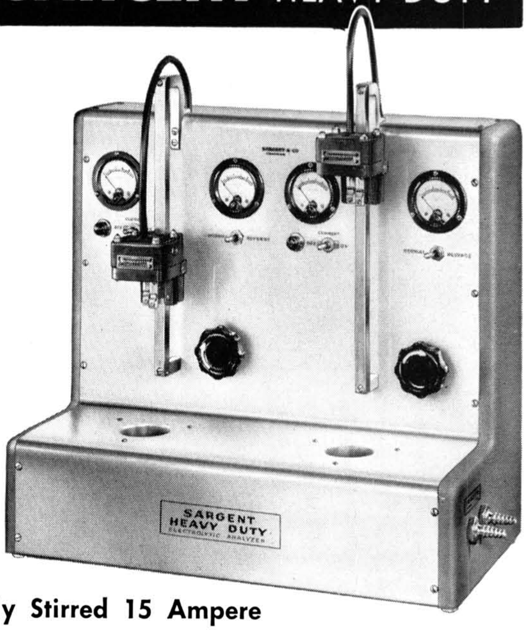

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A Theory of the Kinetics of Formation of Anode Films at High Fields[1]

J. F. DEWALD

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

ABSTRACT

A theory is presented for the anodic oxidation of metals such as tantalum and aluminum. The theory of Mott and Cabrera has been extended to include effects of space charge on kinetics of the process in the highfield case.

The behavior of these systems is shown to depend critically on a dimensionless factor, δ, which is determined by the lattice and energy parameters and also by the experimental conditions.

For δ very small, corresponding to small space charge, the kinetic equation reduces to that of Mott and Cabrera. For large values of δ a very similar equation results which, however, contains only the parameters of the bulk oxide. For intermediate values of δ, complex behavior is predicted. In particular, the temperature independence of Tafel slope observed for tantalum is shown to be a consequence of the theory for certain reasonable choices of the parameters.

INTRODUCTION

Mott and his coworkers have developed theories for the oxidation of metals, and in a recent paper (1) they derive equations for the rate of growth of "very thin" films. Under this heading they treat the growth of films under electric fields so high that the drift velocity is no longer linear in the applied field. They use the data of Gunterschultze and Betz (2) for aluminum and calculate lattice parameters and activation energies which seem reasonable. Recently, however, Vermilyea (3) has published data covering a range of temperatures, which dispute some of the predictions of the theory of Mott and Cabrera. Their theory predicts a logarithmic increase of forming field with current density (or rate of formation). The rate of this increase [i.e., the Tafel slope $(d\bar{E}/dlni)$] is predicted to be proportional to the absolute temperature. Vermilyea's data indicate the logarithmic increase as predicted, but the *rate* of increase appears to be temperature independent.

Presented here is an extension of the theory of Mott and Cabrera which was made prior to the publication of Vermilyea's work. Haring (4) has presented a qualitative description of the process, and the present paper puts some of his ideas in quantitative form. The new theory is able to account for all of Vermilyea's data and, in particular, can predict a temperature independent Tafel slope for a wide range of experimental conditions. Two other points of "discrepancy" between theory and experiment were pointed out by Vermilyea. These have been shown (5) to arise from an oversimplified application of the theory.

GENERAL CONSIDERATIONS

The molecular model employed is quite similar to that used by Mott and Cabrera (Fig. 1). Such a potential energy diagram applies to any oxidative process involving the formation of an adherent film. This is true regardless of whether an external voltage is employed (as in the anodic process), regardless of whether the process is a high field or a low field case, and regardless of the detailed mechanism of oxidation.

In the theory of Mott and Cabrera there are four major conditions which affect the rate of oxidation of film-forming metals; two, the activation energy for diffusion of the mobile species (φ) and the jump distance (b), depend only on the nature of the system in question. The other two are the experimentally variable conditions of temperature (T) and electric field (E). The major dependence on these four factors is shown to occur through a term of the form

$$\exp\left[-(\varphi - Ebq)/kT\right]$$

where q = the charge of the mobile ion. This factor represents the fraction of ions which have sufficient kinetic energy to surmount the potential energy barrier (φ). A similar term appears in the extension of the theory made below. This fraction is always finite (above 0°K), so the rate of any thermodynamically feasible oxidation will always be finite. However, if the fraction is very small, because of large activation energy or low temperature, the rate may be so small (e.g., 1 Å/century) that the process could be considered as not occurring at all. The dividing line between this condition and the condition of measurable rate is not very sharp, but as an

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[1] Manuscript received February 25, 1954.

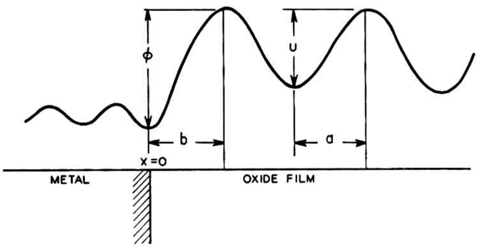

FIG. 1. Schematic potential energy profile of an ion in the high field oxidation process. $x = o$ is taken as the equilibrium position of the ion on the metal surface.

order of magnitude one calculates (this is implicit in what follows below) that if $\varphi - Ebq$ is greater than about 40 kT the reaction is essentially at a standstill, while if it is about 20 kT, reaction will proceed at a very rapid rate.

The high field case of film formation is defined as that in which the field (either inherent in the reaction or applied externally) lowers the potential energy barrier by an amount greater than kT. Thus, if the activation energy is as large as 40 kT, oxidation can occur *only* by a high field process, for if the barrier were not lowered by the field, the rate of reaction, although finite, would be immeasurably small. Conversely, if φ is much less than 20 kT, only the low field case can be dealt with, for any appreciable lowering of the barrier would induce immeasurably *high* rates of oxidation.

In addition to the above requirements, the film and its immediate environment (particularly the film/electrolyte interface) must be capable of withstanding the high fields without breakdown. If, for example, the field were sufficient to oxidize hydroxide ions at the metal/electrolyte interface before it attained a value sufficient to move the ions through the film, then oxidation of the metal would not occur at all except at the immeasurably small rate discussed above. The metal would then be acting simply as an inert oxygen electrode. The intermediate case would correspond to film formation at reduced efficiency, a condition eventually approached by all metal-oxide systems as the thickness of film is increased without limit. In what follows, the currents employed are forming currents and do not include the current which produces side reactions.

Consider the growth of a partly formed film. The film is considered as an ionic lattice of stoichiometric composition[2] through which excess metal ions move under the influence of the field. The ions are assumed to move by jumps from one interstitial position to the next and to be in thermal equilibrium with the lattice at all times.

The assumption that interstitial ions are in thermal equilibrium with the oxide lattice requires some justification. Cabrera and Mott consider that the barrier to ionic motion is at the metal/oxide interface and assume that every ion which escapes from the metal is pulled right across the film. This is not necessarily valid, for when an ion traverses the film it may very well experience deactivating collisions with the lattice and require reactivation before proceeding. Details of this process are quite complex and would require a separate paper for proper consideration. As a first approximation, it is assumed that deactivation occurs immediately after each activation.

Consider first the motion of the ions in the bulk of the film. They obey Boltzman statistics, so for the number of ions per unit volume capable of moving from x to $x + a$ (i.e., concentration of activated ions),[3]

$$n^*(x) = \frac{n(x)}{kT} \int_{U-Eaq}^{\infty} e^{-\epsilon/kT} d\epsilon$$

where: $n(x)$ = concentration of interstitial ions at x; $E = E(x)$ = electric field at x; U = activation energy for motion between interstitial positions in the absence of the electric field; $2a$ = distance between interstitial positions; and q = the ionic charge.

The number which actually move in unit time from x to $x + a$ may be approximated by saying that once an ion becomes activated it crosses the barrier in one vibration period. The number of ions going from x to $x + a/\text{cm}^2/\text{sec}$ is then given by

$$i_+(x) = a\nu n(x) \exp\left[-(U - Eaq)/kT\right]$$

where ν is the vibration frequency of the ion in an interstitial position. Similarly the number going from x to $x - a$ in unit time is given by

$$i_-(x) = a\nu n(x) \exp\left[-(U + Eaq)/kT\right]$$

the only difference being that in this direction the field is retarding the ions; thus a greater activation energy is required. The total current density at x is then given by

$$i(x) = i_+(x) - i_-(x)$$
$$i(x) = 2a\nu n(x) \sinh(Eaq/kT) \exp(-U/kT)$$

So far the treatment is identical with the case of

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[2] X-ray studies are somewhat equivocal on this point.

[3] This equation is not exact for the high field case because, in addition to lowering the barrier, the field causes an effective shortening of the jump distance a. This yields an E^2 term in the lower limit of integration. The equations become much more complex if this term is included, so as a first approximation its effect is neglected.

low field conduction, but from here on there is a striking difference. This is readily seen from the argument of the sinh term. Taking a as of atomic order, e.g., 3 Å, and q as the charge of a Ta^{+5} ion, the argument of the sinh term is about 10^{-5} E at room temperature (with E in practical v/cm). Then only for fields below about 10^{+5} v/cm is the expansion of the sinh Eaq/kT as Eaq/kT valid. This is the usual approximation yielding a current linear in the field.

$$i = nE\mu \tag{I}$$

where μ, the mobility, is field independent.

For high forming fields the linear expansion is not valid. Instead the negative exponential term may be neglected

$$i = n\mu_o \exp{(\beta E)} \tag{II}$$

with $\beta = aq/kT$ and $\mu_o = a\nu \exp{(-U/kT)}$ = constant independent of x and t. Equation (II) relates the forming current density at any point in the film to the concentration of interstitial ions (n) and the electric field (E) at that point.[4] These quantities may or may not vary with time and position in the film. If the current density does not vary with time or position, the film is considered to be in a condition of steady state.

THE STEADY STATE

This concerns the steady-state properties of a film which has been growing for some time at constant rate. The steady state requires that the concentration of ions at any point remain constant with time,[5] i.e., that

$$\frac{(\partial n)}{(\partial t)_x} = 0 = -\frac{(\partial i)}{(\partial x)_t} \tag{III}$$

Using (II) and (III) it is found as a condition on E and n,

$$\frac{(\partial n)}{(\partial x)_t} + n\beta\frac{(\partial E)}{(\partial x)_t} = 0 \tag{IV}$$

but

$$\frac{\partial E}{\partial x} = \frac{4\pi\rho}{K} = \frac{4\pi q n}{K} \tag{V}$$

(where K is dielectric constant of film and ρ is the charge density) so that (IV) becomes

$$\frac{(dn)}{(dx)_{\substack{\text{steady}\\ \text{state}}}} = -\beta\gamma n^2 \tag{VI}$$

with

$$\gamma = \frac{4\pi q}{K}$$

Integrating (VI) gives the dependence of the ion concentration on distance through the film.

$$n = \frac{n_o}{1 + \beta\gamma n_o x} \tag{VII}$$

where n_o = ion concentration at $x = 0$.

Substituting (VII) into (V) and integrating gives for the field at any point x,

$$E = E_o + \frac{1}{\beta}\ln{(1 + \beta\gamma n_o x)} \tag{VIII}$$

Equation (VIII) states that the field at any point in the film is composed of two parts, a surface charge contribution (E_o) and a space charge term. The space charge term arises from the fact that the interstitial ions in transit are not compensated electrically under the conditions of high field formation. In an unbiased condition electrons are present to neutralize the excess charge of the interstitial ions, but at high fields these will all be removed from the film, and the lines of force originating on the interstitial ions must pass through the film ending on the negative ions (probably hydroxide ions) waiting at the electrolyte/film interface.

Cabrera and Mott neglect the space charge contribution entirely. This neglect is based on the assumption that the rate-limiting step in the process of film formation is in getting across the metal/oxide interface. At first glance one might conclude that, if the activation energy for diffusive entrance into the film (φ) is larger than the activation energy for diffusion through the film (U), then the rate-limiting process would always be the motion *across* the interface. Such a conclusion might be valid for the low field case but it is not necessarily valid for the high field case. In the first place, activation energies for *high field conduction* are not φ and U but ($\varphi - Ebq$) and ($U - Eaq$). Thus, if b is greater than a one might anticipate that at sufficiently high fields the entrance barrier would be reduced enough to be less than the barriers inside the film, even though the entrance barrier were higher than the film barrier in the absence of the field.

Even if φ were greater than U, *and* a were greater than b, entrance into the film would not necessarily be the rate-limiting process, for by allowing the film thickness to increase without limit under constant

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[4] For the general nonsteady-state case it is important to distinguish three currents: (*a*) the ion current *in* the film [$i(x, t)$]; (*b*) the ion current across the metal-film interface (i_o); and (*c*) the electron current in the metal (i). These are equal only in steady state.

[5] This is probably not a completely valid requirement since the film is growing at the expense of the metal; thus the reference point ($x = o$) is not stationary. It can be shown, however, that this is only a minor error which may be neglected.

field the increasingly large number of small barriers would eventually predominate over the *single* high entrance barrier (φ) as the rate-determining factor. This treatment makes it possible to predict, for any given set of parameters, at what values of temperature, current density, and film thickness passage through the film becomes rate determining.

The constant E_o in equation (VIII) is given directly by the result of Cabrera and Mott (1) expressed in the form

$$E_o = \frac{kT}{bq} \ln \frac{i_o}{m_s \nu_s} + \frac{\varphi}{bq} \qquad \text{(IX)}$$

where m_s and ν_s are the surface density of metal ions and their vibration frequency. The constant n_o is obtained by equating the current across the interface, i_o, to the current in the film at $x = 0$.

$$i_o = i(o, t) = n_o a\nu \exp\,(-U/kT) \exp\,(E_o aq/kT) \qquad \text{(X)}$$

Substituting (IX) into (X) and rearranging for n_o

$$n_o = \frac{(m_s \nu_s)^{a/b}}{a\nu} \, i_o^{(1-a/b)} \exp\,[(U - a/b\varphi)/kT] \qquad \text{(XI)}$$

At steady state i_o is equal to the external current i so that equations (IX) and (XI) may both be written with i (the directly measurable current) in place of i_o.

Equation (XI) exhibits an interesting dependence of interstitial ion concentration on current density. If the entrance distance, b, is less than the bulk jump distance, a, the steady-state concentration of interstitial ions will decrease as the current density increases. If b is greater than a, increasing current density will cause an increase in the concentration of ions. This behavior is due to the fact that, if the bulk jump distance is greater than the entrance jump distance, an increase in the field will depress the internal barriers more than it depresses the entrance barrier, acting as it does over a larger distance. Thus, a sudden increase in field will cause more ions to leave the film than enter it and, as a consequence, the concentration of ions must decrease with increasing current density. The same argument applies if b is greater than a except that the effect is in the opposite direction.

Finally the average field, $\bar{E}$, which is the experimentally accessible quantity, is evaluated from

$$\bar{E} = \frac{V}{D} = \frac{1}{D} \int_o^D E\,dx \qquad \text{(XII)}$$

where V = voltage drop across the film, and D = film thickness. Substituting (VIII) into (XII), integrating, and replacing n_o by (XI)

$$\bar{E} = E_o + \frac{1}{\beta} \left\{ \left(1 + \frac{1}{\delta}\right) \ln(1 + \delta) - 1 \right\} \qquad \text{(XIII)}$$

with E_o given by (IX) and δ given by

$$\delta = \beta\gamma n_o D = \left[\frac{4\pi q^2}{KkT} \frac{(m_s \nu_s)^{a/b}}{\nu} \right] \cdot e^{(U - \varphi a/b)/kT} D i^{(1-a/b)} \qquad \text{(XIV)}$$

Equation (XIII) gives the dependence of the average steady-state field on the three variables: current density (through E_o and n_o); thickness of film D; and temperature (through E_o, β, and δ). The second term in (XIII) is the space charge contribution to the average field.

The quantity determining the importance of space charge is the dimensionless factor δ. If δ is much less than one, space charge is negligible and the parameters of the metal oxide interface are the rate-determining ones. This is the condition studied by Mott and Cabrera. However, when δ is of the order of one, the neglect of space charge begins to be significant. For δ greater than about 10, the effects of space charge are all important, and the rate of oxidation is determined almost entirely by the bulk properties of the film. This may be seen by approximating the ln $(1 + \delta)$ term in (XIII) either as

$$\ln(1 + \delta) = \delta - \frac{\delta^2}{2} + \cdots$$

for small δ. Or as

$$\begin{aligned} \ln\,(1 + \delta) &= \ln\delta + \ln\,(1 + 1/\delta) \\ &= \ln\delta + 1/\delta - 1/2\delta^2 + \cdots \end{aligned}$$

for large δ. Dropping the second order terms in these expansions, the two limiting cases are given by

$$\bar{E} \approx \frac{kT}{aq} \ln \frac{4\pi q^2}{KkTe\nu} Di + U/aq \quad \delta \gg 1 \qquad \text{(XV)}$$

$$(e = 2.712 \cdots)$$

$$\bar{E} \approx E_o = \frac{kT}{bq} \ln \frac{i}{m_s \nu_s} + \frac{\varphi}{bq} \quad \delta \ll 1 \qquad \text{(XVI)}$$

These equations are of very similar form. For both high and low values of δ the field is logarithmic in current density, and in both cases the *rate* of increase of field with logarithm of current density (the Tafel slope) is proportional to the absolute temperature. For low values of δ the Tafel slope is given by kT/bq, for high values of δ it is given by kT/aq.

Comparison with Experiment

The data of Vermilyea indicate that the Tafel slope is essentially temperature independent over the range from 0° to 80°C. Hence, in this temperature range δ is neither very large nor very small. Therefore the detailed solution with δ of the order of one is required. With reasonable choices of the parameters it is possible to "predict" the existence

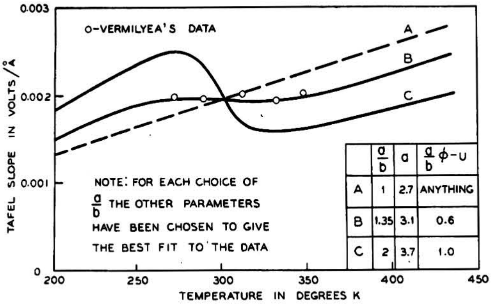

FIG. 2. The variation of Tafel slope with temperature for a 1000 Å film at constant anodizing current density of 100 μa/cm². The curves are drawn, using equation (XIV), to give the best fit to the experimental data of Vermilyea.

of a temperature-*independent* Tafel slope over a fairly wide range of temperature.

The quantity δ depends on film thickness, current density, and on temperature. The first two variations are relatively minor, but the dependence on temperature is quite important. Equation (XIV) shows that the nature of the temperature variation depends upon the sign of the term $[U - a/b\varphi]$. If this term is negative, then δ increases with increasing temperature, and high temperature favors large space charge; the opposite effect would be expected if $[U - a/b\varphi]$ were positive; in such a case the higher the temperature, the lower the space charge.

The effect of temperature on the Tafel slope may be seen by differentiating equation (XIII)

$$\frac{(\partial \bar{E})}{(\partial \ln i)_T} = \frac{kT}{aq}\left[1 + (a/b - 1)\,\frac{\ln(1+\delta)}{\delta}\right] \qquad \text{(XVII)}$$

$$= \text{Tafel slope}$$

Temperature affects the Tafel slope in two ways: directly through T, and indirectly through δ. In general, these two effects act in opposite directions, and when δ is of the order of unity they are of the same order of magnitude. Thus it is possible that the Tafel slope may change very little over the temperature range in which δ is approximately 1. However, certain restrictions must be placed on the parameters. The data available at the present time are not sufficient to evaluate these parameters unambiguously. The reason is that the relative magnitudes of a and b are of critical importance in determining the temperature dependence of Tafel slope. It happens that there are two widely different values of the a/b ratio which allow (with judicious selection of the two activation energies and the absolute magnitude of a) a quantitative fit to all the data available. These values are approximately 1.35 and 0.35. Only for these values of a/b is it possible to achieve a temperature-independent Tafel slope, regardless of the choice of the other parameters. For much different values the Tafel slope either rises continuously with temperature or goes through a maximum and then a minimum before finally rising continuously in the high temperature region.

Using the value 0.35 and determining the other parameters from Vermilyea's data, the resulting value of b places the entrance barrier more than 5 Å away from the equilibrium surface position.[6] This large value is very difficult to visualize, so the conclusion is reached that the correct a/b ratio is 1.35. Experiments at higher temperature are required to verify this conclusion.

Fig. 2 shows the calculated behavior of the Tafel slope for several ratios of a/b in the neighborhood of 1.35. The data of Vermilyea are also shown. As can be seen from equations (XIV) and (XVII), data on the Tafel slope yield information only on the parameters a, b, and the term $(a/b\varphi - \text{U})$. The best fit to the Tafel data are obtained when these parameters have the values 3.1 Å, 2.3 Å, and 0.6 ev, respectively. These values should be viewed as only provisional, since the sensitivity to the parameters is not too large in the plateau region.

The absolute values of φ and U calculated from this model may be obtained by the use of equations (XIII), (XIV), and (IX). Knowing a, b, $(a/b\varphi - \text{U})$, and the experimental variables, δ may be computed from (XIV) and substituted into (XIII). The average field being known from experiment, E_o is determinable; from equation (IX) φ is obtained and thus indirectly U. The values of φ and U so computed are 1.5 and 1.4 ev, respectively, for the best fit to the experimental data.

Extended discussion of the parameter values calculated above is hardly merited in view of their highly provisional character. The only value which seems unreasonable is 3.1 Å for the jump distance a. It appears a little high especially since a is the *half* distance between interstitial sites.

It is not impossible that this large value corresponds to the jump distance from one crystallite to another in the amorphous film. However this may be, it is clear that the data may be empirically represented by the extended theory. The simpler Mott-Cabrera picture cannot do this. The more detailed theory involves two extra parameters, and even though their introduction seems reasonable and was made prior to the experimental observations, further experimental verification would be highly desirable.

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[6] This figure and all the curves and figures presented are based on the assumption of +5 ion charge.

Comments

Equation (XIV) shows that in addition to the temperature variation considered above, δ and thus the average field depends on current density i and film thickness D. The dependence of forming *field* on film thickness is a relatively minor one. It arises from the space charge term, and even for very high values of space charge ($\delta \gg 1$) corresponds to only about 7% increase in field for tenfold increase in film thickness, while for intermediate space charge ($\delta \approx 1$) the increase is only about 2% per tenfold change in thickness. Methods of estimating film thickness are ambiguous because they involve assumptions regarding the constancy of density, surface roughness, anodizing efficiency, and other effects. The data neither indicate nor preclude a variation of field with thickness of the size predicted above.

The variation of δ with current density is such that at both low and high values of δ the field varies logarithmically with current density [Equations (XV) and (XVI)]. In the intermediate range the Tafel plot of $\bar{E}$ vs. ln i should not be exactly linear. Equation (XIII) predicts that the Tafel *slope* should rise with increasing current density when δ is approximately unity. The effect is not very large, however, and might easily be overlooked, even in the absence of complicating effects, if the precision of the data were not good. A linear approximation would probably be assumed by an experimenter unless his data were of a precision of the order of 1%. Complicating factors introduced by heating and electronic currents make the attainment of such precision difficult.

ACKNOWLEDGMENT

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

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Oxidation of Iron-Molybdenum and Nickel-Molybdenum Alloys[1]

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ABSTRACT

Binary alloys of iron and molybdenum (up to 12.5 atomic % Mo) and nickel and molybdenum (up to 19.7 at. % Mo) do not exhibit "catastrophic oxidation" up to 1000°C either in stationary or in flowing atmospheres.

In both systems, MoO_2 and iron molybdate or nickel molybdate are formed in addition to iron oxides or nickel oxide.

Molybdenum significantly decreases the oxidation rate of iron by preventing formation of the cation deficient FeO normally formed on iron above 570°C. The oxidation rate of nickel, however, is affected only to a small extent. Up to 3 at. % molybdenum the rate is slightly increased by the formation of additional vacancies in the nickel oxide, while beyond 12 at. % the oxidation rate is again decreased owing to the densification of the MoO_2 subscale.

INTRODUCTION

In the development of high temperature materials it was hoped that additions of molybdenum would increase the hot strength of heat-resistant alloys. However, molybdenum was found to have a very deleterious effect on the oxidation resistance of such alloys (1–3). Working mainly with the Timken alloy, 16% chromium, 25% nickel, and 6% molybdenum, Leslie and Fontana (1) found that in a static atmosphere at 900°C a 50 g sample would be completely converted to the oxide within 24 hr. This rapid type of oxidation has been termed by them "catastrophic oxidation."

Although there is a difference of opinion as to the exact mechanism of catastrophic oxidation, it is generally agreed that the main cause for this rapid oxidation is the presence of molybdic oxide (MoO_3). The low melting point (795°C) of this oxide and its high vapor pressure (0.25 atm at 1000°C) prevent the formation of the protective oxide which would normally be formed in the absence of MoO_3.

Up to the present, catastrophic oxidation studies have been made mainly on commercial alloys. This paper presents results on the oxidation behavior of laboratory-prepared binary iron-molybdenum and nickel-molybdenum alloys, while the following paper discusses the oxidation behavior of some ternary and quaternary alloys containing nickel or chromium, or both, in addition to iron and molybdenum.

Neither the iron nor the nickel binary alloys exhibited catastrophic oxidation in the temperature range 800° to 1000°C. Maximum molybdenum concentrations were 12.5 and 19.7 at. %, respectively. Tests were made both in still air and flowing oxygen.

Oxidation kinetics of the iron-molybdenum and nickel-molybdenum alloys are presented and a mechanism for their oxidation is proposed.

EXPERIMENTAL

Specimen Preparation

The alloys were prepared by melting 100 g charges in a multiple hearth arc furnace. Their compositions are given in Table I. Electrolytic iron, carbonyl nickel, and molybdenum of over 99.9% purity were used to prepare the melts. Unfortunately, there was considerable tungsten contamination from the tungsten electrode in the preparation of the nickel-molybdenum alloys. However, since tungsten is chemically similar to molybdenum, it is felt that, on an atom to atom basis, tungsten has the same effect as molybdenum. Subsequently all compositions of the nickel-molybdenum alloys are given in atomic per cent of molybdenum plus tungsten.

The 100 g buttons were annealed, ground on two faces, hot rolled, sand blasted, cold rolled, and finally annealed. Final thicknesses were 0.051 cm for iron alloys and 0.064 cm for nickel alloys.

Specimens cut from the rolled strips were cleaned, abraded, and weighed prior to each experiment. In most cases, specimen dimensions were approximately 1.3 x 3.2 cm with an apparent surface area of about 9 cm². Some specimens were electropolished, but no appreciable differences were observed in the experimental results.

Procedure.—Oxidation of the alloys was deter-

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[1] Manuscript received March 22, 1954.

TABLE I. *Composition of alloys*

Iron-molybdenum

Alloy	Mo (at.%)
100	Puron
101	0.64
102	1.83
103	2.61
104	5.29
105	6.16
106	6.51
107	12.5

Nickel-molybdenum

Alloy	Mo (at.%)	W (at.%)	Mo + W (at.%)
900	—	0.32	0.32
902	1.73	0.02	1.75
903	2.87	0.13	3.00
904	6.60	0.20	6.80
905	13.0	<0.17 (spect.)	13.1
906	20.5	<0.18 (spect.)	20.6

mined by continuous weighing. Samples were suspended from a Chain-O-Matic balance into a vertical tube furnace. The sensitivity of the balance was approximately 0.1 mg, while the furnace temperature deviation was less than 2°C.

The sample was inserted into the 1-in. reaction tube while a reducing mixture of hydrogen and helium was being passed through. Construction of the reaction tube insured preheating of the gases. After equilibrium temperature had been reached and the zero time weight had been recorded, the hydrogen flow was interrupted and dried oxygen was introduced. The oxygen flow was maintained at 1 l/min. In a few cases, specimens were oxidized in untreated air both flowing and stationary. Weight measurements were made periodically, in some cases up to 60 hr.

The validity of measuring oxidation rate by following weight increase due to oxygen pickup may be questioned. If volatile MoO_3 is formed by the oxidation reaction, the measured weight increase would not correspond to the amount of oxygen reacted in the oxidation process. To be certain that this factor is not appreciable, metal loss measurements as well as weight gain measurements were made on some of the alloys. Fig. 1 shows such measurements for the Fe-6.16 at. % Mo alloy. After the initial period of formation, the ratio of measured oxygen pickup to amount of metal oxidized ($\Delta m_o/\Delta m_M$) remains at about 0.420.

As shown later, the bulk oxide on this alloy at 1000°C consists primarily of Fe_3O_4 and Fe_2O_3. The ratio of oxygen to metal in these oxides is 0.382 and 0.430, respectively. If there had been an appreciable amount of volatile MoO_3 formed, $\Delta m_o/\Delta m_M$ would have been significantly lower than 0.420.

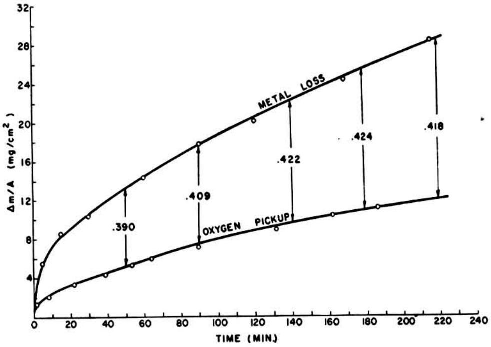

FIG. 1. Comparison between metal loss and oxygen pickup. Fe-6.16 at. % Mo alloy, 1000°C, air flow 3 l/min. Numbers indicate ratio of oxygen pickup to metal loss $\Delta m_o/\Delta m_M$.

To check further the possibility of the formation of volatile MoO_3, three of the iron alloys were first oxidized and then reduced again in H_2. The difference in initial and final weight indicates the amount of molybdenum oxidized to the volatile MoO_3. The following results were obtained at 1000°C:

Atomic % Mo	Oxidation time, min	Metal oxidized, mg/cm²	Mo lost, mg/cm²
0.64	120	25.25	nil
6.16	170	24.30	nil
12.5	205	24.70	0.37 (max)

It can be concluded from these results that iron-molybdenum alloys up to 12.5 at. % do not form any appreciable amount of volatile MoO_3 when oxidized at 1000°C. This is in agreement with the early findings of Scheil and Kiwit (4) who reported that iron-molybdenum alloys up to 6.1 at. % molybdenum did not produce any observable amount of MoO_3 when heated to 1200°C. Similar tests with some of the nickel alloys indicated that nickel-molybdenum alloys up to 19.7 at. % Mo also do not form volatile MoO_3 during the oxidation process.

RESULTS

Iron-Molybdenum

Disregarding the initial period of oxide formation, the oxidation of iron and iron-molybdenum alloys up to 12.5 at. % Mo can be described by

$$\frac{\Delta m}{A} = k\sqrt{t} + C \qquad \text{(I)}$$

where: $\frac{\Delta m}{A}$ = oxygen pickup per unit area of the metal, mg/cm²; k = parabolic rate constant mg/cm² min$^{\frac{1}{2}}$; t = oxidation time (min); and C = constant.

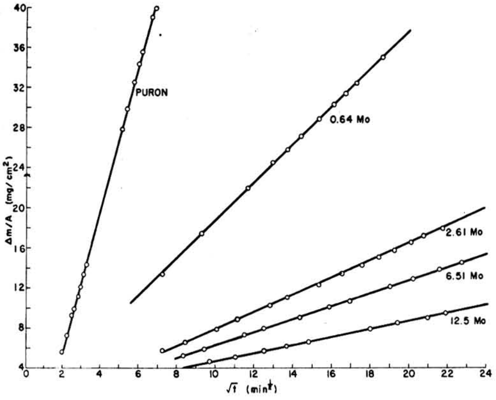

FIG. 2. Oxidation of iron and iron-molybdenum alloys, 1000°C, O_2 flow ~ 1 l/min.

This relation indicates that diffusion of metal ions and oxygen ions through the oxide film is the rate-controlling factor in the oxidation of the alloys as well as of pure iron.

Fig. 2 and 3 show the typical parabolic oxidation of some alloys at 1000°C. Values of the rate constants k, in Table II, were obtained from the slopes of these curves. They were determined from single runs of about 8-hr duration. In all cases they are the lowest values of k found during this investigation and are considered the most reliable values. Rate constants obtained from duplicate runs vary less than 25% from the values given in Table II.

Samples held in flowing or stationary air oxidized at a slightly faster rate, but there was no evidence of catastrophic oxidation.

There is a significant decrease in the oxidation rate as molybdenum is added with the greatest effect for the first few per cent. This is shown clearly in Figure 4.

Since the parabolic rate constant is directly re-

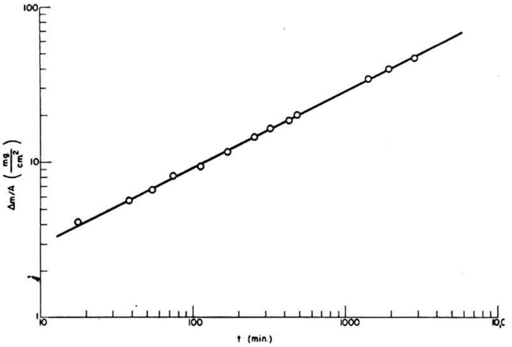

FIG. 3. Oxidation of Fe-6.16 at. % Mo alloy, 1000°C, O_2 flow ~ 1 l/min.

TABLE II. *Parabolic rate constants*

Iron-molybdenum

Mo (at.%)	Temp,°C	k 10^3 (g/cm² min$^{1/2}$)	k' 10^8 (g²/cm⁴sec)
Puron	1000	7.1	80.0
0.64	1000	1.9	5.8
1.83	800	0.11	0.019
	850	0.17	0.048
	900	0.33	0.18
	950	0.67	0.75
	1000	0.98	1.60
2.61	1000	0.86	1.22
5.29	1000	0.66	0.72
6.16	800	0.12	0.23
	850	0.18	0.56
	900	0.30	0.15
	950	0.55	0.50
	1000	0.83	1.15
6.51	1000	0.65	0.66
12.5	800	0.12	0.022
	850	0.18	0.053
	900	0.23	0.087
	950	0.31	0.16
	1000	0.40	0.26

Nickel-molybdenum

Mo + W (at.%)	Temp,°C	$k \cdot 10^3$ (g/cm² min$^{1/2}$)	$k' \cdot 10^{10}$ (g²/cm⁴sec)
Carbonyl Ni*	1000	0.119	2.38
0.32	1000	0.182	5.52
1.75	1000	0.195	6.35
3.00	1000	0.214	7.64
6.8	1000	0.219	7.99
	900	0.109	1.98
	800	0.0426	0.302
13.1	1000	0.210	7.33
	904	0.108	1.93
	800	0.0438	0.319
20.6	1000	0.117	2.28

* Value reported by Pfeiffer and Hauffe (8).

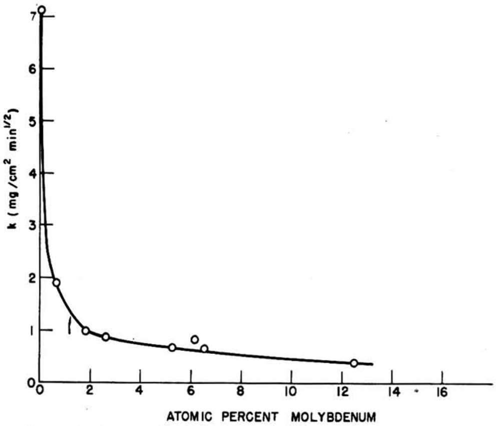

FIG. 4. Parabolic rate constant of iron-molybdenum alloys as a function of composition, 1000°C, O_2 flow ~ 1 l/min.

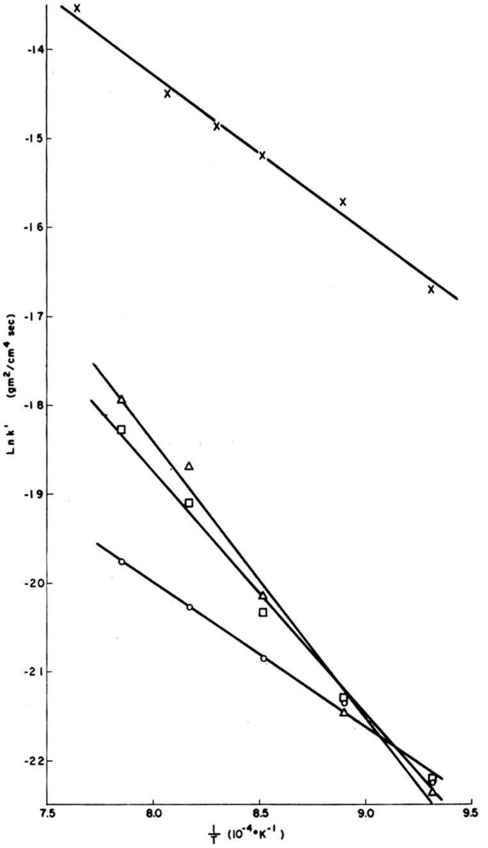

FIG. 5. Temperature dependence of the parabolic rate constant of iron and iron-molybdenum alloys. ×, Fe; △, 1.83 at. % Mo; □, 6.16 at. % Mo; ○, 12.5 at. % Mo. Data for Fe taken from Davies, Simnad, and Birchenall (5).

TABLE III. *Values of A and Q*

Mo (at.%)	*A* (g² cm⁻⁴sec⁻¹)	*Q* (cal/mole)
	Iron-molybdenum	
0*	1.2	36,000 ± 1000
1.83	1.0 × 10³	63,000 ± 3000
6.16	23.0	54,000 ± 2000
12.5	1.2 × 10⁻³	33,000 ± 1000
	Nickel-molybdenum	
High purity Ni†	9.6 × 10⁻⁴	41,200
6.8	0.036	44,500 ± 1400
13.1	0.015	42,600 ± 1300

* Obtained from data of Davies, Simnad, and Birchenall (5).

† Gulbransen and Andrew (550°–700°C) (9).

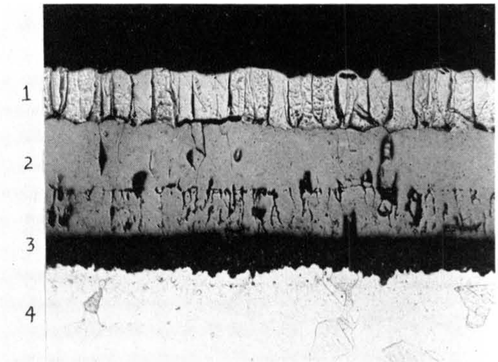

FIG. 6. Oxide layers on Fe-0.64 at. % Mo alloy. Oxidized 350 min at 1000°C. 1—Fe_2O_3; 2—Fe_3O_4; 3—MoO_2 + $(Fe_xMo_y)O$. 4—Alloy. (250× before reduction for publication.)

TABLE IV. *X-ray diffraction analyses of the innermost oxide layer formed on the* Fe-*12.5%* Mo *alloy at 1000°C*

d	Phase	hkl
6.32	D.O.*	001
5.00	D.O.	100
3.54	D.O.	110
3.41	MoO_2	
3.15	D.O.	002
2.78	MoO_2	
2.52 2.50	D.O.	200
2.42	MoO_2	
2.22	D.O.	210
2.11	D.O.	003
2.00	?	
1.72 1.71 1.70	MoO_2	
1.57	D.O.	203 301
1.48	D.O.	302

* D.O. = double oxide of molybdenum and iron. Possible structure: tetragonal a_o = 5.00; c_o = 6.32.

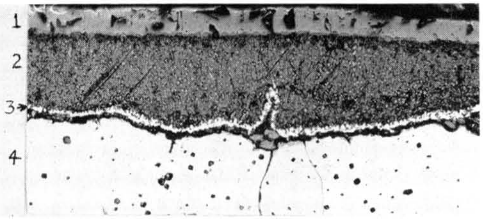

FIG. 7. Oxidation of iron (Puron) at 1000°C. 1—Fe_3O_4; 2—FeO + precipitated Fe_3O_4; 3—gold marker; 4—Fe.

lated to the diffusion constant of the ions through the oxide layers, the Arrhenius relationship

$$k' = Ae^{-Q/RT} \ (k' \text{ in g}^2/\text{cm}^4 \text{ sec}) \qquad \text{(II)}$$

is expected. As Fig. 5 shows, iron-molybdenum alloys do exhibit this relationship although there is some scatter in the data. The temperature dependence of the oxidation of pure iron, as determined by Davies, Simnad, and Birchenall (5), is included as a reference. The values of A and Q computed by the least square method are tabulated in Table III. There is a large variation in both A and Q. Since the oxidation process of these alloys involves the migration of ions through a complex multiple oxide structure, no attempt was made to interpret the mechanism of the oxidation in terms of the A and Q values.

Oxide structure and mechanism of oxidation.—Photomicrographs and x-ray diffraction studies of the oxide revealed three distinct layers (*see* Fig. 6). The outer layer consists of Fe_2O_3, the middle layer of Fe_3O_4, and the inner layer of a mixture of MoO_2 and an unidentified phase presumably a double oxide of molybdenum and iron. X-ray diffraction results of the inner scale on the 12.5 at. % alloy are given in Table IV. Indexing of the "d" values corresponding to the double oxide suggests, as one possibility, a tetragonal structure with $a_o = 5.00$ Å and $c_o = 6.32$ Å. A chemical analysis of the oxide layers on the 12.5 % alloy oxidized at 1000°C gave the following compositions:

Layer	Mo (at.%)	Fe (at.%)
Bulk oxide (Fe_3O_4 + Fe_2O_3 layer)	0.37	44.0
Inner scale [(MoO_2) + ($(Fe_xMo_y)O$)]	20.4	14.6

Thus, there is a large accumulation of molybdenum in the form of MoO_2 and $(Fe_xMo_y)O$ at the oxide-alloy interface and there is no indication of an FeO layer which would normally constitute the major portion of the oxide formed on pure iron (*see* Fig. 7).

These two phenomena are interrelated. When the specimen is initially exposed to the oxygen, iron oxide forms since the oxygen affinity of iron, as shown in Table V, is larger than that of molybdenum. Since the diffusivities of molybdenum and iron are not infinite, the metal surface soon becomes depleted in iron and enriched in molybdenum. Following Wagner's (6) analysis and assuming ideality, the equilibrium condition for the coexistence of an oxide AO and the alloy A_xB_y is that

$$N^2_{(i)A} P_{o_2(i)} = \pi_{ox} \qquad \text{(III)}$$

where: $N_{(i)A}$ = mole fraction of A in the metal core at the alloy-oxide interface; $P_{o_2(i)}$ = oxygen partial pressure at the interface alloy-oxide; and π_{ox} = dissociation pressure of AO.

Considering then the two reactions

$$2Fe + O_2 = 2FeO$$

$$Mo + O_2 = MoO_2$$

it is seen that MoO_2 can form at the expense of FeO when

$$\frac{\pi_{FeO_2}}{N^2_{(i)Fe}} = \frac{\pi_{MoO_2}}{1 - N_{(i)Fe}} \qquad \text{(IV)}$$

Using the calculated dissociation pressures shown in Table V, $\pi_{FeO} = 0.169 \times 10^{-14}$ and $\pi_{MoO_2} = 2.99 \times 10^{-14}$, the mole fraction of iron at which MoO_2 can form (under ideal conditions) is 0.21. As soon as the iron content in the alloy at the alloy-oxide interface falls below this value, MoO_2 can replace FeO along the interface, physically separating the FeO from the metal core. Thermodynamically, FeO is unstable if not in contact with iron and, therefore, converts to Fe_3O_4.

TABLE V. *Dissociation pressures of some oxides at 1000°C**

FeO	1.69×10^{-15}
Fe_3O_4	6.08×10^{-15}
Fe_2O_3	8.77×10^{-14}
MoO_2	2.99×10^{-14}
MoO_3	3.24×10^{-12}
Cr_2O_3	4.84×10^{-24}
NiO	1.67×10^{-10}

* Free energy data from Kubaschewski and Evans (7).

The fast rate of oxidation of pure iron is a result of the rapid migration of iron ions through the layer of FeO which can exist with a large amount of metal vacancies. If the growth of FeO can be prevented as in the present case, the rate of oxidation will be decreased appreciably. In view of these considerations, it is now understandable why the rate of oxidation of iron is affected most by the addition of the first few per cent molybdenum. As long as the molybdenum content is in excess of that which can be removed by diffusion into the interior, MoO_2 and

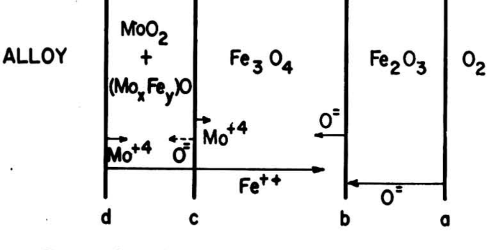

FIG. 8. Growth of oxide layers on iron-molybdenum alloys.

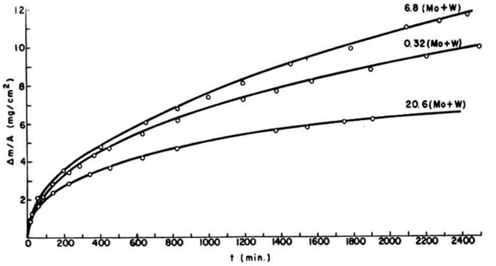

FIG. 9. Oxidation of nickel-molybdenum alloys, 1000°C, O_2 flow ~ 1 l/min.

$(Fe_xMo_y)O$ form, separating the FeO from the metal base. This separation is further facilitated by the formation of the molybdenum-iron double oxide that probably has a still lower dissociation pressure than MoO_2.

The mechanism of the oxide growth on the alloy is postulated to be similar to that on pure iron as described by Davies, Simnad, and Birchenall (5). By means of radioactive tracers, they showed that iron ions migrate through the FeO layer, oxygen ions through the Fe_2O_3 layer, and both iron and oxygen ions migrate through the Fe_3O_4 layer. Oxygen ion migration in the Fe_3O_4 layer, however, is reported to be small in comparison to the iron migration. The oxide growth can be described as shown schematically in Fig. 8. Oxygen ions migrating through the Fe_2O_3 layer and iron ions migrating through the Fe_3O_4 layer react at interface "b" according to

$$2Fe_3O_4 + O \rightarrow 3Fe_2O_3$$

$$4Fe_2O_3 + Fe \rightarrow 3Fe_3O_4$$

At interface "c," additional Fe_3O_4 can be formed by the direct combination of iron and oxygen ions

$$3Fe + 4O \rightarrow Fe_3O_4$$

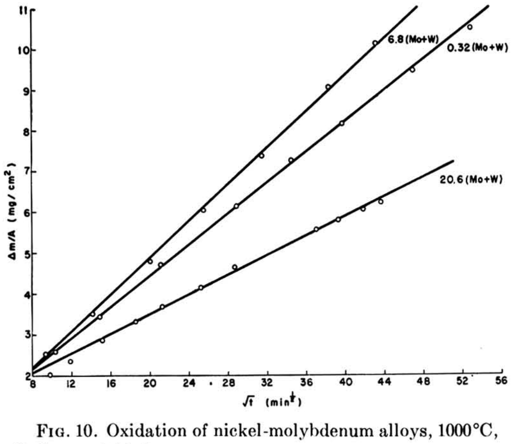

FIG. 10. Oxidation of nickel-molybdenum alloys, 1000°C, O_2 flow ~ 1 l/min.

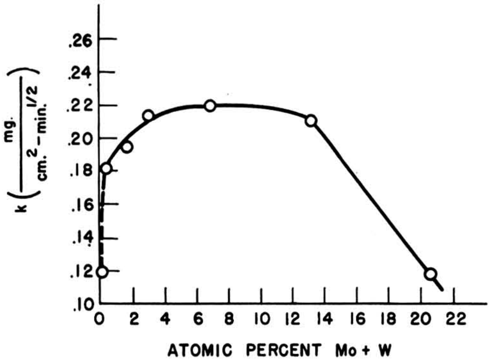

FIG. 11. Effect of composition on the parabolic rate constant of nickel-molybdenum alloys at 1000°C.

The formation of MoO_2 probably occurs at "d," the metal-oxide interface.

Migration of molybdenum ions in the iron oxide at 1000°C is only slight, as the chemical analysis of the bulk oxide indicates. However, at temperatures above 1000°C, the diffusivity of the molybdenum ions and their solubility in the iron oxides becomes great enough for appreciable amounts of molybdenum ions to reach the oxide-oxygen interface where they form the volatile MoO_3.

Nickel-Molybdenum

Fig. 9 shows typical oxidation curves for some of the nickel-molybdenum alloys. Except for the initial period, the oxidation rate is again parabolic and the temperature dependence of the rate constants follow the Arrhenius relationship.

The rate constants k evaluated from curves such as shown in Fig. 10 are summarized in Table II. These constants correspond to single runs of at least 8-hr duration. Duplicate runs indicated a variation in k of less than 10%.

Fig. 11 shows the effect of composition on the parabolic rate constant at 1000°C. The value of k for carbonyl nickel as reported by Pfeiffer and Hauffe (8) is included for reference. As can be observed, the rate increases up to 3 at. % Mo + W, then remains approximately constant up to 12%, beyond which it decreases again. However, the over-all effect of composition is relatively small.

The temperature dependence of k for two of the alloys is shown in Fig. 12. The calculated A and Q values for these two alloys are given in Table III. The values for high purity nickel (550°–700°C) as found by Gulbransen and Andrew (9) are included for comparison. Although there is an appreciable change in A, the heat of activation, Q, for the two alloys varies only by a small amount from that of pure nickel.

Structure of the oxidation product.—Oxidation of the alloys produced three distinct layers, as shown

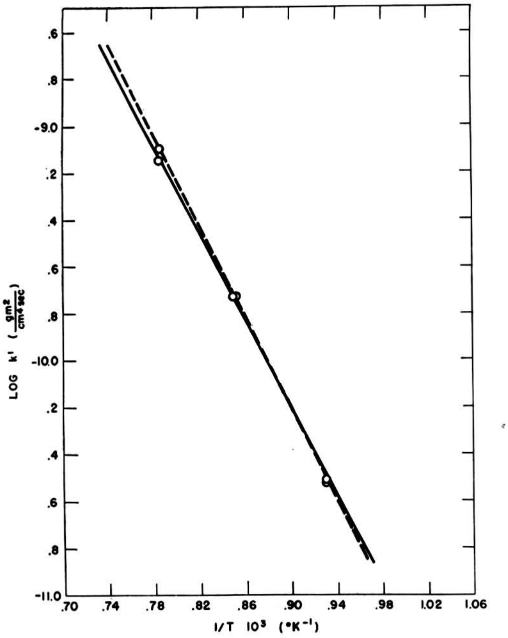

FIG. 12. Temperature dependence of the parabolic rate constant of nickel-molybdenum alloys. – – –, 6.8 (Mo + W); ——13.1 (Mo + W).

schematically in Fig. 13. In addition to the external scale of NiO and $NiMoO_4$, a subscale of MoO_2 is formed.

Oxides were identified both visually and by x-ray diffraction. By means of a tapered section (10× mechanical magnification), as shown in Fig. 14, the thin layer of $NiMoO_4$ could be resolved. The subscale region is also clearly evident.

Little is known concerning nickel molybdate. It is soft, light green in color and is readily formed by heating a mixture of NiO and MoO_3 above 500°C. X-ray diffraction from the $NiMoO_4$ produced by oxidation was identical to that produced synthetically. The "d" values of the major diffraction lines obtained on a Philips x-ray spectrometer are listed in Table VI. Due to line broadening and distortion, their accuracy is somewhat limited. It was not possible to identify the crystallographic structure, but it seems to fit most closely into the tetragonal system.

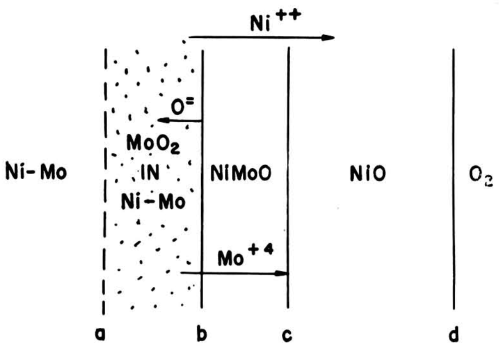

FIG. 13. Oxide growth on nickel-molybdenum alloys

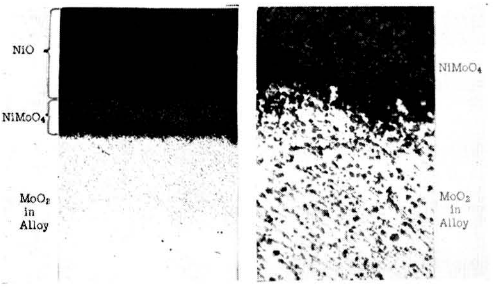

FIG. 14a (left). Alloy 904 (6.8 at. % Mo + W), 63 hr at 1000°C. (1000× before reduction for publication); FIG. 14b (right). Alloy 904 (6.8 at. % Mo + W), 63 hr at 1000°C. (5000 × before reduction for publication).

$NiMoO_4$ is stable up to 1150°C, above which it decomposes, releasing MoO_3. As reported by Spretnak and Speiser (10), upon cooling, $NiMoO_4$ undergoes polymorphic changes causing appreciable volume changes. This behavior is well illustrated by the fact that, upon cooling, the scale on the oxidized alloys shatters off violently from the metal core. It was, therefore, difficult to prepare the specimens for metallographic observation.

Mechanism of oxide growth.—Since the oxidation rate of the molybdenum-containing alloys is not appreciably different from that reported for carbonyl nickel, it can be assumed that the rate-determining factor of the oxidation process is still the diffusivity of the nickel ions in the nickel oxide layer.

It was estimated that the proportion of $NiMoO_4$ in the bulk oxide increases as a function of molybdenum content from about 2 to 5% in the 3.0% alloy to about 20% in the 20.6% alloy. If the dif-

TABLE VI. *Interplanar spacings of* $NiMoO_4$, *and relative intensity of diffraction*

d	I/I_{max}
6.12	0.61
3.80	0.09
3.48	0.33
3.07	1.00
2.73	0.57
2.31	0.18
2.19	0.20
2.06	0.50
1.91	0.15
1.71	0.15
1.63	0.10
1.60	0.18
1.50	0.25
1.46	0.10

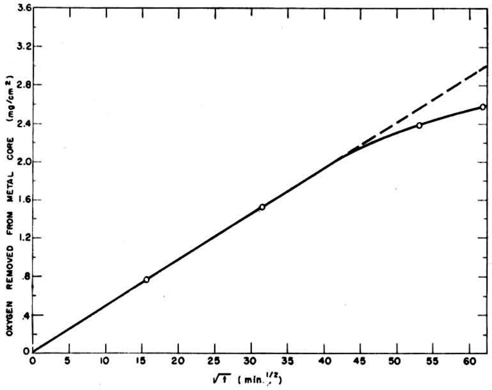

FIG. 15. Growth of the subscale on alloy 904 (6.8 at. % Mo + W), 990°C, O_2 flow ~ 1 l/min.

fusivity of nickel ions in the molybdate were less than that in NiO, an appreciable change in the parabolic rate constant as a function of composition would have been observed. The small variation in the heat of activation, Q, further indicates that the controlling factor, i.e., the diffusion of nickel ions through the NiO, is the same in both nickel and nickel-molybdenum alloys up to 13.1 at. % molybdenum.

Formation of $NiMoO_4$ and MoO_2 can, therefore, be considered as secondary effects. After reaching stationary equilibrium, the oxide growth continues as shown schematically in Fig. 13. Nickel ions diffuse through the $NiMoO_4$ and NiO layers to form new NiO at the interface "d." Concurrently, molybdenum ions migrate through the $NiMoO_4$ layer and react with the NiO at the interface "c" according to

$$Mo + 4NiO \rightarrow NiMoO_4 + 3Ni \qquad (IV)$$

The rate of growth of the $NiMoO_4$ layer depends on the molybdenum content of the alloy. At the interface "b," oxygen diffuses into the interior, the driving force being the difference between the dissociation pressure of $NiMoO_4$ and the oxygen partial pressure in the alloy.

Since the decomposition pressure of MoO_2 is much less than that of NiO (3.0×10^{-14} as compared to 1.7×10^{-10} at 1000°C), MoO_2 precipitates in the alloy matrix.

Growth of the subscale is determined by the difference in the rate of formation of the external scale and the diffusion rate of oxygen. A parabolic relationship is therefore expected. This relationship has been confirmed by Rhines (11) and Thomas (12).

The oxygen uptake by the metal core of the 6.8% alloy is plotted as a function of $t^{\frac{1}{2}}$ in Fig. 15. Each point was determined separately by removing the oxygen with hydrogen after the external scale was removed. Except for deviations at the longer times, a parabolic relationship is observed. Some error is introduced because dissolved oxygen as well as the combined oxygen is removed. Incomplete reduction of the MoO_2 may also have occurred.

Decrease of the oxidation rate of the 20.6% molybdenum alloy may be due to densification of the subscale which hinders migration of nickel ions from the interior. In effect, the contact area between the metal core and the external scale is decreased.

Increase in the oxidation rate of the alloys containing up to 13.1% Mo is probably due to the incorporation of some molybdenum ions in the NiO lattice. Being deficient in cations, ions of higher valency will introduce further metal vacancies in the nickel oxide structure, thus increasing the rate of oxidation. This behavior has been found in the investigations of Wagner and Ziemens (13) and Pfeiffer and Hauffe (8).

As the temperature is increased, the solubility of molybdenum in NiO becomes greater. Some of the molybdenum ions reaching the oxygen interface form MoO_3 which evaporates from the surface. Thus, at 1118°C, the 20.6% Mo alloy formed 0.00062 g/cm² of MoO_3 during 65½ hr of oxidation.

CONCLUSION AND SUMMARY

Molybdenum significantly alters the high temperature oxide structure on iron and nickel. Because of the low solubility of molybdenum in NiO and in the iron oxides, molybdenum-rich oxide layers of MoO_2 and molybdate are formed. The volatile MoO_3, however, is prevented from forming, and catastrophic oxidation does not occur. Molybdenum considerably decreases the oxidation rate of iron. Molybdenum enrichment at the alloy surface during the early part of the oxidation prevents the development of the cation deficient FeO layer normally found on iron above 570°C. The oxidation process is now controlled by the migration of iron and oxygen through the more diffusion-resistant Fe_3O_4 and Fe_2O_3 layers.

The oxidation rate of nickel is affected to a much lesser degree by the addition of molybdenum. Up to 13.1 at. %, the rate is slightly increased by formation of additional vacancies in the NiO lattice due to dissolved molybdenum atoms. Above 13.1%, the MoO_2 subscale becomes dense enough to hinder migration of nickel ions and the rate, therefore, decreases again. It is postulated that the controlling step in the oxidation process is still the migration of nickel ions across the NiO layer. The small change in oxidation rates and in experimental heats of activation of the alloys supports this.

ACKNOWLEDGMENT

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

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Catastrophic Oxidation of Some Molybdenum-Containing Alloys[1]

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ABSTRACT

When nickel or chromium is added to binary iron-molybdenum alloys, catastrophic oxidation occurs in certain concentration regions. Chromium is more effective than nickel in inducing this rapid type of oxidation.

Catastrophic oxidation occurs because of the formation of liquid MoO_3 along the metal-oxide interface. This is preceded by the cracking of the chromium or nickel-containing oxide.

Catastrophic oxidation does not occur with alloys containing large amounts of nickel.

INTRODUCTION

Catastrophic oxidation of certain alloys containing appreciable amounts of molybdenum has been reported. It is postulated that this rapid type of attack is due to the formation of MoO_3. The presence of other volatile and low melting oxides such as V_2O_5 (670°C), Bi_2O_3 (820°C), PbO (888°C), WO_3 (1473°C), and mixtures of these oxides can also induce this type of attack in the absence of molybdenum (1–4).

While several workers (2–4) are of the opinion that catastrophic oxidation stems from the presence of a liquid oxide layer, none of these postulates how the liquid film is formed and what the oxidation process is, in the case where the liquid oxide is formed by the alloying element.

This paper presents results on the oxidation of some molybdenum-containing materials and proposes a mechanism of catastrophic oxidation. A previous paper (5) showed that binary nickel-molybdenum alloys up to 30% (weight) molybdenum and binary iron-molybdenum alloys up to 20% molybdenum do not oxidize catastrophically at 1000°C. In both cases, MoO_2 and molybdate, in addition to nickel oxide or iron oxide, are formed during oxidation. To induce catastrophic oxidation, additions of nickel or chromium or both were made to binary iron-molybdenum alloys.

EXPERIMENTAL

Specimen preparation.—All alloys were prepared by arc melting in a multiple hearth arc furnace. Their nominal compositions are given in Table I. In most cases, nominal compositions deviate less than 5% from analyzed compositions. Nominal weight percentages are used throughout this paper.

The 100 g alloy buttons were ground on two faces, hot rolled, sand blasted, cold rolled if possible, and finally annealed. Specimens 0.020 in.–0.040 in. were cut from the rolled strips.

Procedure.—Oxidation of the alloys was determined by measuring the weight loss of the metal. Weighed specimens were placed in covered alundum filtering crucibles which were seated in a 4-in. diameter crucible furnace. The purpose of the alundum crucible was to minimize contamination from the neighboring samples and from the fire brick plug. Oxygen was passed through the crucible furnace at a rate of about 2 l/min to insure against oxygen depletion. The temperature was constant to better than ±5°C.

The amount of metal oxidized was determined as follows. After the bulk oxide was removed, the weight of the metal core with the residual oxide remaining on it was determined. The residual oxide was then reduced in hydrogen and its original weight was calculated by assuming that the oxide contained 25% oxygen.

RESULTS

When nickel was substituted for iron in the 20Mo80Fe alloy, the striking and unexpected result shown in Fig. 1 occurred. Up to 10% nickel there is only a small change in the oxidation rate; beyond 15% there is a sudden increase with a maximum at about 25Ni. At this composition the oxidation is about 15 times as fast as with the 20Mo70Fe10Ni alloy. Beyond 25Ni, the oxidation rate again decreases rapidly, approaching that of the 20Mo70Fe10Ni alloy at 40Ni. An increase to 60Ni gives only a small change in the oxidation rate.

Additions of chromium to the iron-molybdenum alloys initiated rapid oxidation even more readily. Only small amounts of chromium in the order of 5% are sufficient to accelerate attack. Some alloy samples oxidized completely in the 2-hr testing

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[1] Manuscript received March 22, 1954.

TABLE I. *Loss of metal by oxidation during 2 hr at 1000°C*

Alloy	$\Delta m/A$ (mg/cm²)
20Mo80Fe	16.1
20Mo75Fe5Ni	9.4
20Mo70Fe10Ni	9.9
20Mo65Fe15Ni	27.9
20Mo60Fe20Ni	93.8
20Mo55Fe25Ni	152.5
20Mo50Fe30Ni	46.2
20Mo40Fe40Ni	11.2
20Mo20Fe60Ni	3.7
25Ni75Fe	18.2
25Ni70Fe5Mo	14.1
25Ni65Fe10Mo	23.9 (uneven attack)
25Ni45Fe30Mo	122.5
50Ni20Fe30Mo	4.8
10Mo5Cr85Fe	128.5 (uneven attack)
5Mo15Cr80Fe	112.0 (uneven attack)
15Mo10Cr75Fe	>365.0 (completely oxidized)
25Cr75Fe	1.0
20Mo5Cr75Fe	31.3
15Mo15Cr70Fe	>361.0 (completely oxidized)
20Mo10Cr70Fe	>198.0 (completely oxidized)
5Mo25Cr70Fe	1.0
10Mo25Cr65Fe	58.4 (uneven attack)
30Mo5Cr65Fe	34.3
40Ni20Mo35Fe5Cr	10.3
40Ni20Mo30Fe10Cr	10.5
40Ni20Mo20Fe20Cr	5.7

period. The effect of chromium additions in excess of 25% could not be evaluated because of the difficulty of fabrication of the alloys.

The three quaternary alloys containing 40% nickel did not exhibit catastrophic oxidation even though the chromium and molybdenum content were as high as 20% each.

Table I lists for every alloy the amount of metal oxidized during 2 hr of oxidation at 1000°C. These values are plotted as a function of composition in Fig. 2, the shaded areas indicating the regions of catastrophic oxidation.

The amounts of metal oxidized as given in Table I are single values, not averages. Several duplicate determinations were made on most of the alloy samples, generally giving a reproducibility of within 30% of the reported values. Where oxidation was not uniform, the reproducibility was less satisfactory; however, the relative degree of attack was not altered. Several of the duplicate determinations were made in the absence of other specimens and in different furnaces. In all cases the amount of oxidation was within the normal reproducibility, indicating that contamination of one sample by another was kept to a minimum.

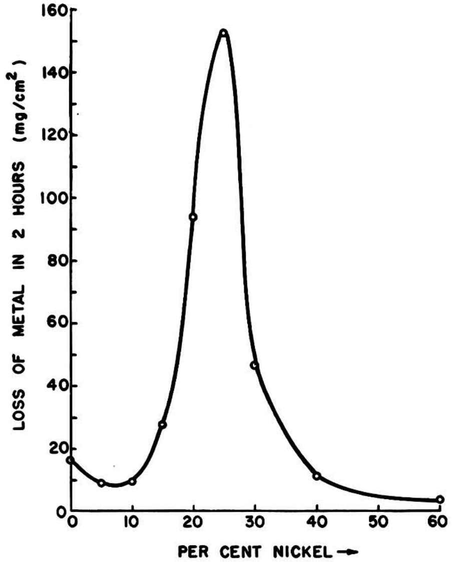

FIG. 1. Oxidation of 20MoFeNi alloys, 1000°C. (Nickel is substituted for iron in the original 20Mo80Fe alloy.)

MECHANISM OF CATASTROPHIC OXIDATION

The results on oxidation of iron-molybdenum alloys and on nickel-molybdenum alloys, as reported previously (5), show that, due to the enrichment of molybdenum, MoO_2 is formed immediately adjacent to the alloy surface. As long as the MoO_2 is prevented from oxidizing to MoO_3, normal oxidation

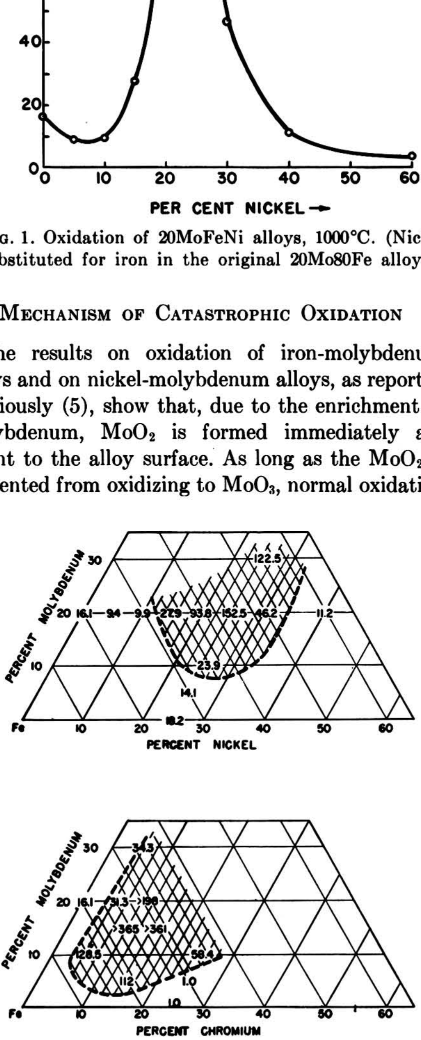

FIG. 2. Oxidation of FeMoNiCr alloys. Numbers indicate weight loss per unit area after 2 hr at 1000°C. Shaded areas indicate regions of rapid oxidation.

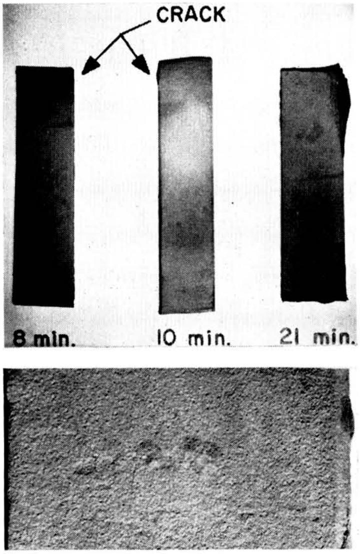

FIG. 3. Crack formation in oxide on 15Mo75Fe10Cr Alloy at 1000°C. Top, crack growth as a function of time. (2× before reduction for publication); bottom, oxidation after 8 min. (10× before reduction for publication.)

occurs. However, as soon as the MoO_2 has access to a large supply of oxygen, the low melting and highly volatile MoO_3 is formed.

The simplest method of supplying the MoO_2 layer with oxygen is by means of a crack or pore in the main oxide. Pore formation does occur with the MoFeCr alloys as shown in Fig. 3. After the initially very rapid formation of the chromium-rich oxide, a crack appears exposing the molybdenum-enriched surface. Molten MoO_3 is formed which penetrates along the metal-oxide interface. Being less noble, the chromium and iron in contact with the MoO_3 constantly reduces the MoO_3 according to

$$MoO_3 + 2Fe \rightarrow Mo + Fe_2O_3$$

$$MoO_3 + 2Cr \rightarrow Mo + Cr_2O_3$$

Being an excellent flux, liquid MoO_3 probably dissolves the chromium and iron oxide at the $MoO_{3(l)}$-metal interface. Fluxing is further facilitated by the released heat of formation of chromium and iron oxide which tends to increase the temperature at the metal-$MoO_{3(l)}$ interface. The dissolved iron and chromium oxide nucleate and precipitate again in

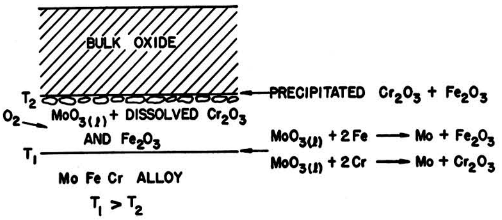

FIG. 4. Mechanism of catastrophic oxidation

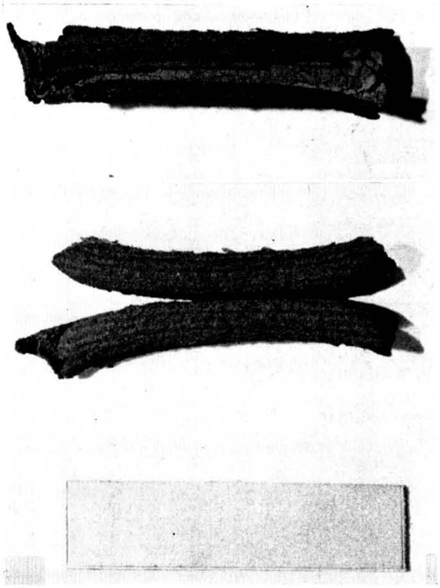

FIG. 5. Oxidation of 15Mo75Fe10Cr alloy, 2 hr at 1000°C. Top, top view of oxidized specimen; center, side view of oxidized specimen; bottom, original alloy specimen. (1½× before reduction for publication.)

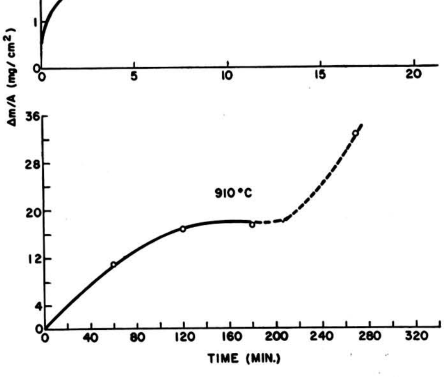

FIG. 6. Oxidation of 15Mo75Fe10Cr alloy

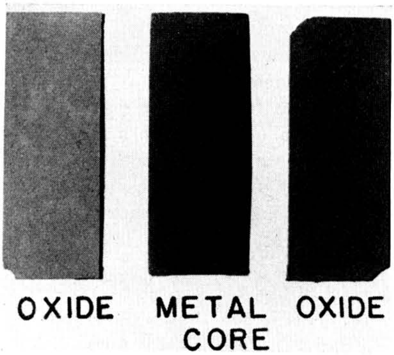

FIG. 7. Oxidation of 20Mo55Fe25Ni alloy, 2 hr at 1000°C. (1½× before reduction for publication.)

the cooler region near the $MoO_{3(l)}$-bulk oxide interface. This process is shown schematically in Fig. 4.

Thus, the original crack or pore is never healed and both MoO_2 and Mo have continual access to the oxygen. As the metal is oxidized along the edges, the oxide curls up until, after complete oxidation, it appears as shown in Fig. 5.

The cracking of the Cr-rich oxide is in agreement with the findings of McCullough, Fontana, and Beck (6). In their investigation on the oxidation of some stainless steels, they found that at 980°C there was an abrupt increase in the oxygen pickup after an initial period ranging from 10 to 45 min. At 925°C the time to rupture increased to about 4 hr.

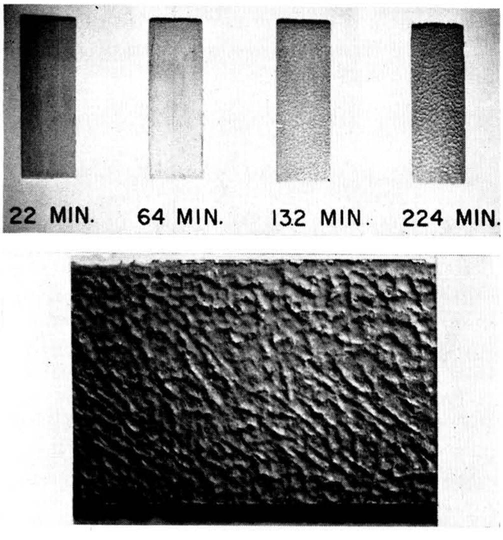

FIG. 8. Surface roughening of the 20Mo55Fe25Ni alloy during oxidation at 910°C. Top, surface roughening as a function of time (1× before reduction for publication); bottom, surface after 224 min. (5× before reduction for publication.)

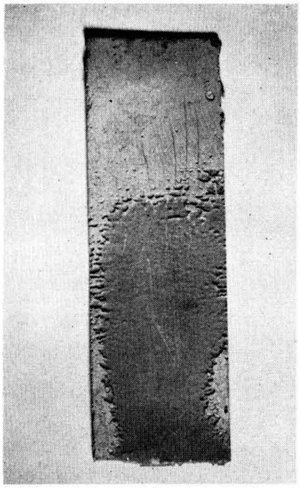

FIG. 9. Nonuniform oxidation of 20Mo55Fe25Ni alloy, 1 hr at 1000°C.

Fig. 6 shows the weight loss of 15Mo10Cr75Fe alloy as a function of time at 1000° and 910°C. The two curves show clearly the abrupt increase of oxidation after about 15 min at 1000°C and 3½ hr at 910°C.

That the crack should appear at the edges is quite reasonable. Presumably the crack formation comes by the stress relieving of the compressed oxide. Since a sharp edge offers little constraint, the oxide tends to pull away from it.

X-ray analysis of the oxide formed on the MoFeCr alloys showed it to consist of a mixture of Fe_2O_3 and Cr_2O_3. No $Cr_2O_3 \cdot FeO$ could be detected even before the cracking of the oxide occurred.

At first it appeared that the mechanism of the rapid oxidation of the MoFeNi alloys was different from that of the MoFeCr alloys. Oxidation is less violent and more uniform. This behavior is shown

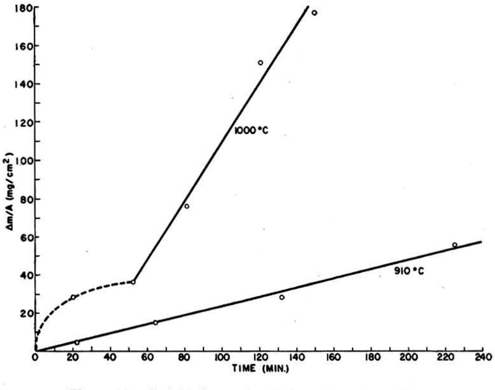

FIG. 10. Oxidation of 20Mo55Fe25Ni alloy

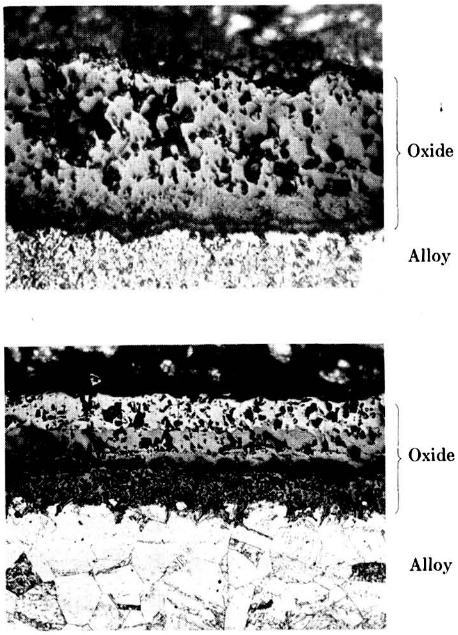

FIG. 11. Top, rapid oxidation, oxide on 30Mo45Fe25Ni alloy, 2 hr at 1000°C; bottom, retarded oxidation, oxide on 5Mo70Fe25Ni alloy, 5 hr at 1000°C. (250× before reduction for publication.)

in Fig. 7 which shows the metal core and the two oxide plates removed from the 20Mo55Fe25Ni alloy sample after 2-hr oxidation at 1000°C. However, it was noticed that in many cases the oxide had pulled away slightly from the edges. An investigation of the surface of the 20Mo55Fe25Ni alloy after oxidation for varying periods at 910°C revealed the development of a rough and ridged surface (Fig. 8) suggesting the presence of a liquid phase. It was also observed that at the higher temperature (1000°C) some areas of the specimen were sometimes attacked more severely than others, as shown in Fig. 9.

In view of these facts, it is believed that the oxidation mechanism is similar to that of the MoFeCr alloys. After the metal surface is enriched by molybdenum, oxygen obtains access to the surface and forms liquid MoO_3. The MoO_3 penetrates along the metal-oxide interface, constantly being reduced by the less noble iron and oxidized by the ambient oxygen. Iron oxide is dissolved in the molten MoO_3 and re-precipitated along the bottom surface of the bulk oxide (see Fig. 4). Since nickel is considerably more noble than molybdenum, nickel-rich ridges form on the surface. This process can, therefore, be described as a selective oxidation by a liquid phase. Since the oxygen affinity of chromium is much larger than that of iron, it can readily be seen that the oxidation of the chromium alloys should be much more violent.

An effort was made to indicate more clearly the cracking or pore formation of the oxide on the 20Mo55Fe25Ni alloy. Oxidation measurements as a function of time were made at both 910° and 1000°C (Fig. 10). Neither of the two measurements definitely shows that cracking occurs, although there is good indication of it at 1000°C. At both temperatures, oxidation is linear with time.

Returning to Fig. 1, it can now be said in view of the foregoing discussion, that in the range of 15–35% nickel, a liquid film of MoO_3 is formed, while with the other compositions molybdenum is prevented from oxidizing to the higher oxide. The difference between the oxide structure of the 45Fe30Mo25Ni alloy exhibiting rapid oxidation and the 5Mo70Fe25Ni alloy exhibiting normal oxidation is pointed out in Fig. 11. The normally oxidized sample exhibits the MoO_2 rich oxide layer adjacent to the alloy surface, while the rapidly oxidized sample shows only one homogeneous layer.

The question remains why there is a critical nickel composition range in which rapid oxidation occurs. It was hoped that x-ray diffraction analysis of the oxides formed on the alloys would give some clue. However, the main oxide on all the MoFeNi alloys beyond 10% nickel consisted primarily of a Fe_3O_4 spinell-type phase. The oxide is undoubtedly $(Fe, Ni)O \cdot Fe_2O_3$ with nickel ions replacing the ferrous ions as the nickel content is increased.

An analysis of the oxide formed on the 20Mo55Fe25Ni alloy (maximum rate of oxidation) gave the following composition:

	Wt %
Fe	50.0
Ni	22.0
Mo	0.7
O	balance

This indicates that the ratio of nickel to iron is practically the same in the oxide as in the alloy. Furthermore, with this amount of nickel in the oxide, ferrous ions are almost completely replaced by nickelous ions and $NiO \cdot Fe_2O_3$ is formed exclusively. It is, therefore, hypothesized that $(FeNi)O \cdot Fe_3O_4$ is more prone to cracking than is the pure $FeO \cdot Fe_3O_4$. The oxide on the alloys with more than 35% nickel may still crack, but now the alloy surface below the oxide is sufficiently diluted with nickel to prevent the formation of MoO_3. This reasoning is in agreement with results reported previously (5) that nickel-molybdenum alloys containing 30% molybdenum do not exhibit catastrophic oxidation.

Similar analysis is extended to the three MoFeNiCr alloys. If the oxide does crack, there is enough nickel on the alloy surface to prevent the formation of liquid MoO_3, and healing of the crack can occur.

SUMMARY AND CONCLUSIONS

When chromium or nickel is added to binary iron-molybdenum alloys which oxidize normally, catastrophic oxidation can occur within certain composition regions. Chromium induces catastrophic oxidation more readily than nickel.

It is postulated that immediately after the initial oxidation, the metal surface becomes enriched in molybdenum. The oxide on the alloy cracks, allowing the formation of liquid MoO_3 along the alloy oxide interface. $MoO_{3(l)}$ constantly oxidizes the iron and chromium in the alloy to Fe_2O_3 and Cr_2O_3. Fe_2O_3 and Cr_2O_3 dissolve in the MoO_3 and re-precipitate along the MoO_3-bulk oxide interface. Healing of the crack cannot, therefore, occur.

When the alloy contains a sufficient amount of nickel, formation of MoO_3 is prevented in a similar manner as in the nickel-rich nickel-molybdenum alloys. Thus, MoFeNiCr alloys with 40% nickel and 20% molybdenum do not oxidize catastrophically. These alloys may be of industrial use.

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

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Controlled Preparation and X-Ray Investigation of Cadmium Sulfide[1]

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ABSTRACT

A furnace for the controlled preparation of cadmium sulfide (CdS) by the vapor phase method is described. A constant rate of evaporation of the cadmium metal is maintained so that any changes in the ratio of Cd to S, or in the speed of reaction, can be made. Inserts fitted into the reaction tube allow the quick removal of the formed CdS without cooling the furnace. By controlled operation of the reaction furnace, a uniform crystal habit was obtained. X-ray diffraction analysis showed lattice imperfections to be present in CdS and CdSe crystals.

INTRODUCTION

Hexagonal α-CdS, which occurs in nature as the mineral "greenockite," has been grown in the form of crystals by Lorenz (1) by the reaction of Cd vapor with H_2S. Frerichs (2) modified the method by heating Cd metal in a small porcelain boat in a quartz tube to about 800°–1000°C. Cd vapor was driven by a slow stream of H_2 to the zone of the tube where it could react with a stream of H_2S. Yellow hexagonal needles and flat ribbons of photoconducting CdS were obtained.

Replacing H_2 as diluting gas by argon (3), it was found advisable to use baffles in the reaction tube to minimize concentric currents. To grow larger crystals (10 x 5 x 3 mm), CdS powders (4) or the small crystals obtained by the vapor-phase method can be recrystallized (5). This requires a prolonged heat treatment under hydrogen sulfide pressure at temperatures of about 1000°C.

The vapor phase method has the advantage that most impurities are separated by fractionate sublimation (2) so that purification of the Cd metal is not necessary. The light sensitivity of such crystals, however, was found (5–7) to be very different, even for crystals of the same batch. Besides the desirable highly sensitive crystals with high dark resistance up to 10^{13} ohms, crystals with high resistance but low sensitivity were also found. Some crystals show red fluorescence when exposed to ultraviolet light, while others show no evidence of luminescence.

It is conceivable that these differences of the properties of the samples are caused by uncontrolled changes of stoichiometric composition, changes in the impurity content, or possible faults of crystal growth.

With previously described methods of preparing CdS by vapor-phase reaction it is difficult to control the rate of evaporation of the Cd metal. The evaporation depends not only on the temperature, but also on the continuously changing surface areas of the molten metal in the boat. The first-formed small crystals, therefore, are exposed to vapors of Cd and H_2S in an almost continuously changing ratio. For that reason, an improved reaction furnace was desirable. The features of the new design should lead to a better controlled and more continuous preparation of CdS which would establish the conditions under which certain crystal habits, fine powders, or large uniform crystals can be obtained.

It is comparatively easy to control the temperature of the reaction and the flow of H_2S into the reaction furnace. The problem of operating the furnace at a constant ratio of Cd to S, therefore, is concentrated in the problem of keeping the rate of evaporation of the Cd metal constant.

REACTION FURNACE

The ceramic parts of the furnace are made in the form of two halves between which the glass part can be inserted. To obtain a constant rate of evaporation of the metal, Cd is heated to a temperature slightly above the melting point in a U-shaped Vycor tube (Fig. 1) by a heating coil (F1). The right branch (F2) of the U heats molten Cd up to its boiling point at 767°C. A constant level of the boiling metal surface is maintained by making the left branch (F1) several times larger than the boiler tube (F2). The surface of the molten metal in the left branch must be protected by an inert gas to prevent oxidation. Cd metal can be added to (F1) even during the operation of the furnace through the V-shaped part of the Cd reservoir. A thermocouple placed in the molten metal (Th1) measures and regulates the temperature.

The heating coil for the boiler (F2) covers only a small part of the metal column but all of the gas

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[1] Manuscript received April 12, 1954.

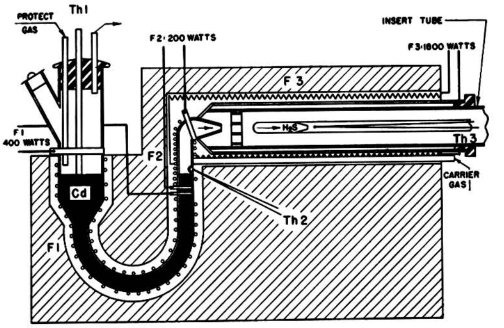

FIG. 1. Reaction furnace

TABLE I. *Dimensions of the reaction furnace*

	Furnace	(F1) Reservoir	(F2) Boiler	Reaction zone (F3)
Length, in.	22	9	3	15
Width, in.	10	2	3/8	2
Height, in.	18			
Heating coil, watts		400	200	1800

space above it. Above the boiling surface of the metal Cd vapors can be mixed with preheated carrier gases such as N_2, H_2, or He. Purified and dried carrier gas enters the furnace through a tube at the extreme right and is heated by the heating elements of the furnace (F3).

The carrier gas serves several purposes. It maintains a constant flow of the vapor in the direction of the reaction zone in (F3) and protects the boiling metal surface so that no H_2S reaches the boiler. It also enables one to change and adjust the amount of Cd entering the reaction tube. The temperature regulation of the boiler (F2) is, of course, very critical, if constant conditions are to be maintained. The hot junction of a thermocouple (Th2) is, therefore, placed in a cavity of the Vycor tube above the boiling metal; the temperature of the boiling metal is controlled by an automatic regulator.

To measure the amount of Cd vapor entering the reaction tube (F3), the following method was adopted. By maintaning a constant temperature in (F2) the level of the boiling metal was kept in coincidence with a mark made on the right branch of the U-shaped Vycor tube. This is possible, if, from time to time during the experiment, solid Cd metal is added to the left branch of the tube. The weight of the metal needed to keep the level in (F2) at a constant height is, of course, equivalent to the amount of Cd entering the reaction tube during the experiment.

A hole drilled into the ceramic insulating material and covered by mica permits observation of the level of liquid Cd (F2) from the outside of the furnace.

The mixture of Cd vapor and carrier gas enters the reaction zone (F3) through a knee and a perforated porcelain plate. The latter serves as a baffle to distribute the gases equally over the space and as an obstacle for the H_2S to avoid blocking of the Cd vapor outlet.

Inside the reaction tube an insert is held tightly by ground glass, whereas outside of the furnace the two tubes are tightened by a rubber ring. The insert tube contains the thermocouple (Th3) for regulating the temperature in (F3) and the H_2S inlet. The length of the H_2S inlet was chosen so that the dried gas already possesses the temperature of (F3) when it enters the reaction zone. The insert tube is used for quick removal of the formed CdS, and several of these inserts are kept in stock.

Formation of CdS can be stopped instantly by cooling the boiling metal at (F2) with cold air, and quick changes of the insert tubes can be made without opening or cooling the furnace. The furnace could be made to work continuously, if a worm screw or a belt is built in to remove the formed material. Some technical data on the furnace are given in Table I.

Depending upon the temperature and the gas

TABLE II. *Spectrographic analysis*

Elements	Raw material Cd metal for No. 32,33	CdS No. 32 (Table III)	CdS No. 33 (Table III)	Commercial luminescent pigment	Limit of detection
Ca	0.01–0.1	0.001–0.01	0.001–0.01	0.001–0.01	0.0001
Mg	0.001–0.01	0.001–0.01	0.001–0.01	0.001–0.01	0.0001
Si	0.001–0.01	0.001–0.01	0.001–0.01	0.001–0.01	0.0001
Zn	0.001–0.01	—	—	0.05–0.1	0.01
Cu	0.01–0.1	0.0001–0.001	0.0001–0.001	0.0001–0.001	0.0001
Sn	0.01–0.1	—	—	—	0.0001
Ag	0.0001–0.001	*	*	*	0.0001
Fe	0.001–0.01	*	0.0001–0.001	*	0.0001
Ni	0.01–0.1	—	—	—	0.0001
Pb	0.05–0.1	—	—	—	0.0001

* Element may be present at concentrations near the limit of detection.

TABLE III. *Preparation conditions and crystal habit*

Preparation condition	CdS No. 33	CdS No. 32
Temp, °C		
Melting reservoir (F1)	400	400
Cd boiler (F2)	690	870
Reaction zone (F3)	950	950
Gas flow, mole/min		
Carrier gas N_2	0.75×10^{-2}	6.4×10^{-2}
Cd vapor	0.668×10^{-3}	17.9×10^{-3}
H_2S	0.444	0.018
Mole ratio Cd to S	1:664	1:1.005
Crystal habit	100% type [1] homogeneous needles	85% type [2] 15% type [3], [4], [5] polycrystalline rods

flow maintained, a laboratory furnace of the given dimension yields about 5–200 g CdS/hr.

In fact, the method described for the controlled reaction of vapors might be generally useful for the manufacturing of other substances (ZnS, CdO, PbSe) by vapor-phase reactions.

SPECTROGRAPHIC ANALYSIS, CRYSTAL HABIT, AND X-RAY DIFFRACTION

In Table II, spectrographic analyses of the Cd metal used and the CdS prepared from it in the furnace are compared with the analysis of a commercially available, luminescent CdS obtained by wet chemical preparation methods. The analysis is in accord with Frerichs' (2) observation about purification during the process. It also shows that the vapor-phase method leads to substances which are at least as pure as those obtained by wet chemical methods.

By a morphological investigation of CdS crystals grown by the vapor-phase method, five different "types" were observed and correlation was found (6) between electrical properties and habit. According to this investigation, 500 crystals collected from 15 different batches occurred as needles, ribbons with rectangular and oblique striations, and twins with the following frequencies: type [1] thoroughly homogeneous needles 17%; type [2] ribbons with rectangular striations 18%; type [3] ribbons with oblique striations 25%; type [4] twins of [1]; and type [5] twins of [3]. Relatively poor photoelectric properties were found on crystals of types [4] and [5].

The present experiments, however, performed under controlled conditions, demonstrate that the crystal habit of CdS can be determined by properly chosen preparation conditions. Conditions for obtaining type [1] crystals or a mixture of several types are shown in Table III for two characteristic experiments. With a mole ratio of Cd to S of 1:664 and flow rates of 0.44 moles H_2S/min only single crystal needles of type [1] were grown with an average needle size of 6 to 15 x 2 x 3 mm. Although some dendritic hollow needles were observed, which is characteristic of rapid crystal growth, the batch was very homogeneous with respect to the crystal habit. By x-ray and optical methods the needle axis was found to be the c-axis of the crystal. Much smaller crystals of all types and microcrystalline rods were obtained with a mole ratio of approximately 1:1 and flow rates of 0.018 H_2S/min. Most of the crystals show dendritic habit and parallel striations in the direction of the c-axis. The twinning of the oblique striated crystals (type [3]) occurs along the bypyramide face. Spectrographic analysis of the two samples (Table II) does not show significant differences in the impurity content.

The reproducibility for obtaining crystals of type [1] of the same size, purity, and x-ray characteristics was confirmed in several experiments. The uniformity of the crystals within the batch (CdS No. 33 in Table III) was found to be maintained over a length of 7½ in. in the reaction zone of (F3) (Fig. 1), corresponding to the temperature gradient along the furnace.

Grinding of luminescent materials is usually accompanied by a loss of luminescent properties of the material. In the case of hexagonal ZnS, the destruction by pressure was explained (8) by the introduction of lattice defects and the formation of electron traps. The concentration of these imperfections was thought to be so small as to escape detection by routine x-ray and electron diffraction methods.

This is different in the case of α-CdS. If powder x-ray diagrams with Cu-Kα radiation are taken of the unground but sieved CdS crystals, the photograph shows sharp lines up to the highest reflection angles and good resolved α_1-α_2 doublets. Grinding in a mortar, as done for routine x-ray diffraction work, changes the color of the substance from light

TABLE IV. *d-Values of the low angle lines in* CdS *and* CdSe

α-CdS		α-CdSe	
d in Å	rel. intensity	*d* in Å	rel. intensty
22	1		
11.5	3		
10.5	7	11.38	5
7.98	3	8.26	1
6.75	5	7.02	3
6.19	4	6.47	3
5.70	4	5.93	3
5.32	−1		
4.92	−1		
4.58	1		
4.11	1		
3.74	1		
3.55 ($10\bar{1}0\alpha$-CdS)	8	3.68 ($10\bar{1}0\alpha$-CdSe)	6

yellow to brown. At the same time, the x-ray diagram of the ground material shows a loss of intensities and line broadenings with increasing diffraction angles. The intensities of (0002), $(10\bar{1}2)$, and $(11\bar{2}2)$ are increased. Since the grinding of such substances in a mortar usually does not achieve particle size below 1 μ the line broadening and intensity losses at higher angles are caused solely by mechanical deformation faulting (plastic deformation) (9).

If x-ray diagrams of hexagonal CdS are carefully examined, many of them show additional rings in the low angle region. Rings were found in the powder diagrams of commercial luminescent CdS pigments (Table II), in the ground substance of a commercially available single crystal photocell, in samples prepared by precipitating cadmium chloride solutions or reacting solid cadmium acetate with H_2S, and in many of the vapor-phase prepared crystals. The sharpness of these additional diffraction rings varies, and sometimes diffuse bands are formed. The measured *d*-values of these lines in the low angle region are given in Table IV. It is interesting to note that a similar type of diffuse low angle reflection was found in powder diagrams of vapor-phase grown cadmium selenide (CdSe) of equal purity.

A microscopical investigation of the polycrystalline CdS rods grown by the vapor-phase method under the conditions of experiment CdS No. 32 (Table III), shows small, type [1] crystals grown with their c-axis almost perpendicular to the rod axis. A rotation x-ray diagram taken along the rod axis resolved the powder lines of the low angle diffraction into spots of a layer line diagram with an identity period: $I = 22$Å.

In Fig. 2 the fiber diagram is shown of the preferential oriented CdS crystallites in the polycrystalline rod with the layer line diagram of the diffuse low angle spots.

The stoichiometric composition of the samples containing the superlattice was investigated by wet chemical analysis. No evidence, however, was found for the existence of another sulfide or polysulfide. The spectrographic analysis of one of the samples is shown in Table II (CdS No. 32).

More instructive were x-ray diffraction diagrams of the different crystal types [1], [2], [3], and [5]. In the powder diagrams of selected single crystals, low angle lines were observed only on rectangular and oblique striated types [2] and [3] ribbons. The sharpness of low angle rings varied from sample to sample; the broadening, however, seemed to be related to an increase of the diffuse scattering in this area of the photographic film. In diagrams of type [1] crystals, where no low angle lines are detectable, a considerable increase of the scattered intensity could be observed around the incident beam. This indicated the presence of highly dispersed particles (10) in the matrix of hexagonal CdS. If it is assumed, as would seem probable, that it is the same substance which causes low angle diffraction effects, the correlation is immediately evident. The random disorder in type [1] needles appears to be increasingly ordered to a superlattice in the other types.

Single crystal rotation and precession diagrams with exposure times up to 65 hr around the a- and c-axis of type [2] and [3] striated crystals were made. Photographs showed spots in addition to those due to the hexagonal CdS lattice. However, because of the weak intensity and their small number, it is not possible at this writing to give a satisfactory correlation between the superlattice reflections and the orientation of the hexagonal CdS matrix.

Therefore, only tentative interpretations can be given about x-ray effects. The superlattice could be caused by: (*a*) an unknown polymorphic modification of CdS; (*b*) stacking faults (microtwins) (10–13); and (*c*) mechanical deformation faulting (14–15).

The dimensions of the unit cell of α-CdS were determined by measurements of the high angle reflections of the unground but sieved substance only:

$$a_o = 4.132 \pm 0.001 \text{ Å}$$
$$c_o = 6.734 \pm 0.004 \text{ Å}$$

In the limits of the attained accuracy there is no evidence for changes in cell dimensions between samples prepared at different conditions (Table III). The a_o-value confirms the determination of Kröger (17) ($a_o = 4.131$ Å) obtained on a substance of undisclosed origin and purity. The *c*-dimension of Kröger's sample ($c_o = 6.691$ Å) appears, however, to be slightly smaller.

Electrical and photoconducting properties are obviously closely associated with the above described lat-

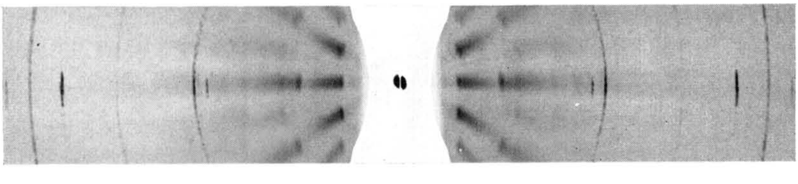

FIG. 2. Fiber diagram of preferential oriented α-CdS crystallites in a polycrystalline rod with the layer lines of the low angle reflections. (Specimen diameter 0.5 mm, rotation along the rod axis, Ni filtered CuK α-radiation.)

tice imperfections of such materials. This and the dependence of the disorder upon the presence of foreign impurities is subject to a further investigation (18).

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

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The Electric Arc as a Circuit Element[1]

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ABSTRACT

Static and dynamic voltage-current characteristics of the electric arc are reviewed, with emphasis on high-current arcs. Typical arc behavior in both d-c and a-c circuits is described with oscillographic examples. The nature and use of some mathematical models for explaining and predicting dynamic behavior of arcs in their connected circuits are considered. Separate contributions to dynamic arc behavior of the arc column and of the electrode regions are discussed.

INTRODUCTION

Since its first scientific study (1) the electric arc has remained an intriguing but rather mysterious phenomenon. The electronic nature of current conduction in the arc was first shown by Weedon (2). Much has been learned since then about the nature of arcs, but they still provide a challenge. Because the theory is incomplete, much of the information about arcs which is available to engineers is necessarily empirical and limited to special cases. Data applicable to higher current arcs are comparatively scarce. This is unfortunate because higher current arcs, which are often of great technical importance, may operate in entirely different regimes with markedly different behavior from arcs with currents near 10 amp, for which the most data are available.

As electrical conductors, arcs exhibit many interesting and often useful properties. These properties may be troublesome, as when they necessitate special stabilizing circuit arrangements for their maintenance in lighting, welding, and furnace applications. Still, their nonlinearity and capacity for rapid change have led to many useful circuit applications in arc oscillators, rectifiers, lightning arresters, and as essential transition elements in power circuit breakers and fuses.

Arcs exist and find important uses in forms and under conditions which are so varied that a general picture is very difficult to present. Even under steady-state conditions, arc behavior depends to a large degree on such factors as electrode material, nature and state of the gas medium, range of current magnitudes, and whether the arc is relatively long or relatively short. Under dynamic conditions, arcs show important additional properties which depend to an essential degree on rates of current change. Often arc behavior is so interrelated with electrical properties of the connected circuit that it is just as responsive to circuit conditions as it is to the physical state of the arc's surroundings.

EMPIRICAL ARC PROPERTIES

Static Characteristic

Perhaps the most familiar electrical property of an arc under steady conditions is given by its so-called inverse volt-ampere characteristic, illustrated by the curve in Fig. 1. This curve is typical for arcs carrying currents of only a few amperes, a range formerly of much practical interest in connection with arc lamps. A number of equations for this characteristic have been derived from experimental studies. The first and best known such equation is that due to Ayrton (3),

$$V_a = A + BL + \frac{C + DL}{I} \qquad [1]$$

expressing the arc voltage, V_a, in terms of the arc length, L, the arc current, I, and the constants A, B, C, and D. This equation was derived primarily for arcs in air with pure carbon electrodes only a few millimeters apart. It was shown by Ayrton and others that arcs with cored carbons, with metal electrodes, or carbon arcs operating in the "hissing" regime occurring at higher currents departed drastically from this relation. Later studies by Nottingham (4, 5) yielded a more generally applicable equation of the same form except that the current was raised to the power n, with n varying according to the anode material from 0.35 for zinc to 1.38 for tungsten. The exponent n was said to vary linearly with the absolute boiling temperature, T, of the anode surface according to the relation

$$n = 2.62 \times 10^{-4}\, T \qquad [2]$$

for arcs in air. For carbon electrodes, n is 1 in agreement with Ayrton. For oxidized copper, n is 0.67. The curve in Fig. 1 has been plotted according to Nottingham's equation, using his values for an arc

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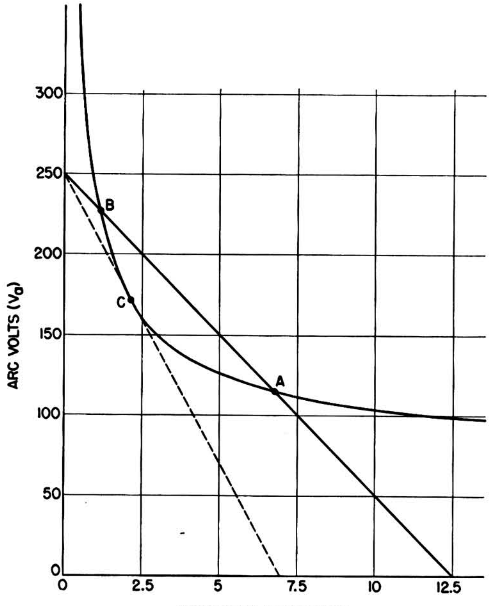

FIG. 1. Static characteristic of a 1.5-in. copper electrode arc in air according to the Nottingham equation.

with oxidized copper electrodes 1.5 in. apart in air. For other gas media, n was different and equation [2] did not apply. The "constant" coefficients in any of the arc equations vary widely with experimental conditions.

Stability requirement.—The first consequence of the falling volt-ampere characteristic is that a steady arc cannot be maintained in a constant emf circuit without a stabilizing series resistance. In Fig. 1 the solid straight line with the equation

$$V_T = 250 - 20\,I \text{ volts} \qquad [3]$$

gives the available voltage at the terminals of an arc in a 250-volt circuit having a resistance of 20 ohms. Steady arc conditions can exist in this circuit only at the intersection points A or B where the arc voltage and the available terminal voltages are equal. The arc can operate *stably*, however, only at point A where a change in the current would give a voltage unbalance tending to restore the equilibrium. At B a current change would give a voltage unbalance tending to further the change, thus prohibiting stable operation at this point. With the conditions illustrated here, lowering the circuit resistance will move the stable operating point A to the right, resulting in a higher arc current and a lower arc terminal voltage. The arc current would tend to increase without limit if the circuit resistance were reduced to zero, this being the condition for a high power "short-circuit." There is also an upper limit for the circuit resistance at this voltage corresponding to the dotted line tangent to the arc characteristic at C. As the series resistance is increased from 20 ohms toward the limiting value, about 36 ohms, the stable operating point A and the unstable intersection B approach each other until they merge at C, destroying the condition for stability. When C is reached the arc will suddenly "go out," the current dropping to zero and the terminal voltage jumping to the open-circuit value of 250 volts. If there is appreciable inductance in the circuit, the rapid current drop at arc extinction will cause a momentary overvoltage to appear at the arc terminals. With highly inductive circuits this overvoltage may reach dangerous values.

In the opening of direct-current circuits at such voltages and currents that an arc is drawn at the switch contacts, extinction of the arc results generally from *lengthening*, which raises the arc characteristic until it becomes tangent to the fixed V-IR line for the circuit.

Long arcs.—If equation [1] holds over a wide range of the variables, and if L is made sufficiently large, the terms involving A and C may be neglected, and the characteristic equation becomes approximately

$$V_a = L(B + D/I) \qquad [4]$$

At small enough currents, the term B in the parentheses may also be neglected, giving

$$V_a = DL/I \qquad [5]$$

or

$$V_aI = DL \qquad [6]$$

the equation for a rectangular hyperbola with the arc characterized simply by a constant required power per unit length. This limiting approximation is often useful in dealing with long arcs at low currents, as, for example, switch or flash-over arcs in high voltage circuits near the minimum currents at which they may be maintained.

High current arcs.—If in equation [1] the current is sufficiently large, the term containing the current becomes relatively small, and the arc voltage becomes a function only of the arc length according to the equation

$$V_a = A + BL \qquad [7]$$

At sufficient lengths the term A may also be neglected, giving an arc voltage proportional only to length,

$$V_a = BL \qquad [8]$$

In practice, this assumption is often adequate for representing such arcs as those in high power circuits under short-circuit conditions, e.g., in power circuit breakers used to clear short circuits.

Under some conditions departure from the assumed arc equation may lead to regimes in which the arc voltage actually rises with arc current. This was observed by Ayrton (3) even at small currents when using cored carbons at short spacings. With long arcs in air at thousands or tens of thousands of amperes, slightly rising volt-ampere characteristics are also observed, due presumably to magnetic effects associated with these currents. Rising characteristics can occur at lower currents also for arcs confined in insulating tubes.

Another noteworthy consequence of the flat or falling volt-ampere characteristic of normal arcs is that such arcs cannot ordinarily be operated in parallel without individual stabilizing resistances.

Nothing has been said so far about the physical basis for the arc characteristic or about numerical values of constants in the arc equations. For short arcs at low currents the observed behavior of these empirical constants is such as to make their theoretical interpretation very difficult, and they vary so much with particular conditions that representative values cannot be stated with any accuracy. For longer arcs, however, some generalizations and some useful values may be noted. For arcs in air at normal pressure and with lengths of a few inches or more, most of the arc voltage exists across the arc column, which has a virtually constant potential gradient. Some 20–40 volts drop (constant A in equation [1]) occurs right at the electrodes and is nearly independent of the arc length. The gradient in the column is almost independent of current magnitude above 50 amp or so and is 12 volts/cm for arcs in the open air (constant B in equation [1]).

Short arcs.—At very short electrode spacings the arc voltage is almost entirely in thin sheaths right at the electrodes and remains virtually constant, being relatively independent of small length variations and of current changes above the range of about 10 amp. The arc characteristic under these conditions is determined principally by the constant A in equation [1]. The constant C always has a relatively small value which may be zero if L is properly measured.

Dynamic Arc Characteristics

With currents changing slowly enough, the voltage drop in an arc follows the static characteristic but, as the current is changed more and more rapidly, hysteresis effects become evident so that the arc voltage departs from the static characteristic by an amount dependent on the rate of current change and the nature and condition of the arc. This behavior is illustrated schematically in Fig. 2 for an arc with the static characteristic given by the hyperbolic curve AB with dotted extensions. Superimposed on a steady current component i_o, for which the steady arc voltage is v_o, is a sinusoidal current oscillation between the limits i_a and i_b. If the frequency of this oscillation, f_1, is low enough, possibly as low as a few cycles per hour for some arcs, the voltage will retrace the single curve AB, faithfully following the static characteristic. At a somewhat higher frequency, f_2, current oscillation between the same limits will cause the arc voltage to follow a near-elliptical loop about the single curve AB. With rising current the voltage will be above AB, returning below it for falling current as shown by the arrow points. At a still higher frequency of current oscillation, f_3, the elliptical curve will change its shape so that its major axis approaches the straight line A′B′, while it still retains its clockwise rotation. At a sufficiently high frequency, f_4, above 100,000 cycles for an arc in air, the arc voltage can be made to follow the single line A′B′ very closely. The arc may be said to have an inherent natural frequency of response, f_o, lying between the values f_2 and f_3. The extreme fre-

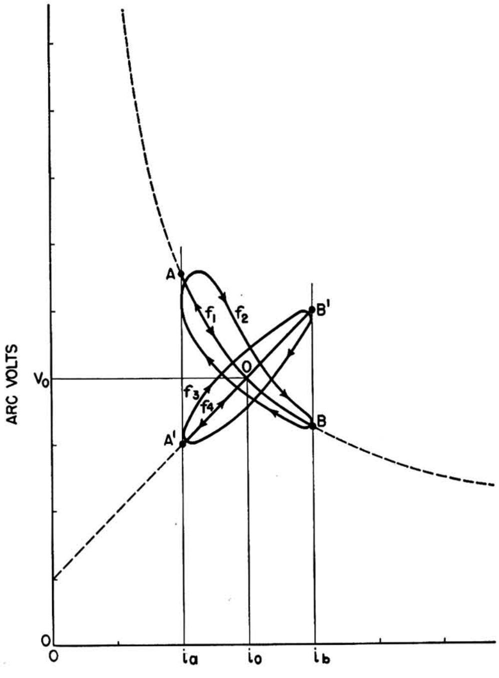

FIG. 2. Dynamic characteristics of arc with current pulsating at successively higher frequencies, $f_1 < f_2 < f_3 < f_4$.

quencies may be characterized by the inequality

$$f_1 \ll f_o \ll f_4 \qquad [9]$$

Since the hysteresis effect appears to reside mainly in the arc column, a line through A′B′ will not generally pass through the origin. This line represents a constant positive arc column resistance, the value of which is the slope dv/di of the line A′B′. This resistance is in series with relatively constant voltage drops at the electrode surfaces. If for very long arcs electrode drops can be neglected, instantaneous resistance of the arc column at a mean current i_o will be given by the slope of a line from the origin to the point O on the static characteristic. The falling *static* characteristic clearly results because the arc resistance adjusts itself to the current when the current changes slowly enough. The factors determining the steady burning voltage of the arc column at any given current are complex, but seem to depend mainly on the convective cooling phenomena in and around the column. The dynamic hysteresis appears to be caused by storage in and near the arc column of energy in the form of heat and ionization associated with the column conductance.

Arc oscillator.—If a large value of capacitance is connected in parallel with an arc, it will tend to hold the arc terminal voltage constant, a condition which can lead to instability. This effect is accentuated if the supply circuit has considerable inductance. Such an arrangement employing a smaller inductance in series with the shunting capacitance has been used as a high power oscillator (6). Approximate analysis of this oscillating circuit, shown in Fig. 3, gives the differential equation for the current i in the parallel LRC circuit,

$$L\frac{d^2i}{dt^2} + \left(R + \frac{dV_a}{di}\right)\frac{di}{dt} + \frac{i}{C} = 0 \qquad [10]$$

the equation for a damped current oscillation with the effective damping resistance inside the parentheses. The term dV_a/di is the slope of the arc volt-ampere characteristic and is negative for the static characteristic. If the frequency of the superimposed oscillating current i is low enough that the mean slope of the *dynamic* characteristic, like the loop f_2 in Fig. 2, is negative, the resistance R can be cancelled and the damping brought to zero, giving the necessary condition for a sustained oscillation at the frequency

$$f = \frac{1}{2\pi\sqrt{LC}} \qquad [11]$$

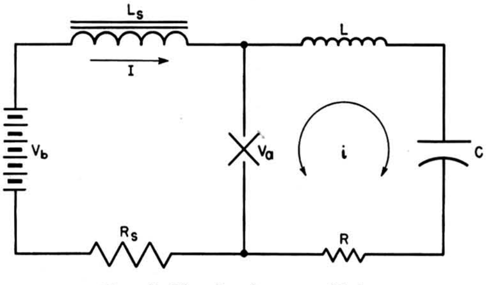

FIG. 3. Circuit of arc oscillator

By operating the arc in a hydrogen atmosphere and subjecting it to a strong magnetic field, such oscillators can be operated at low radio frequencies.

Alternating-current arcs.—The dynamic volt-ampere characteristics of a-c arcs resemble those for the superimposed oscillation in Fig. 2 except, of course, for the relatively larger amplitude, the symmetry of the oscillation about the zero current axis, and the reversal of polarity of the arc voltage with reversal of the current. At relatively low frequencies, say 60 cycles for an arc in hydrogen, the dynamic characteristic may follow the static characteristic closely except in the immediate vicinity of current zero where the voltage reversal occurs.

Fig. 4 shows a volt-ampere plot from the magnetic oscillogram for one half-cycle of a 60-cycle, 1.5-in. arc in hydrogen with the current limited by inductive reactance plus the arc voltage to about 6.4 rms amperes in a 2300-volt circuit. It is evident that the static characteristic is followed closely except for the peculiar hump just after current zero. This

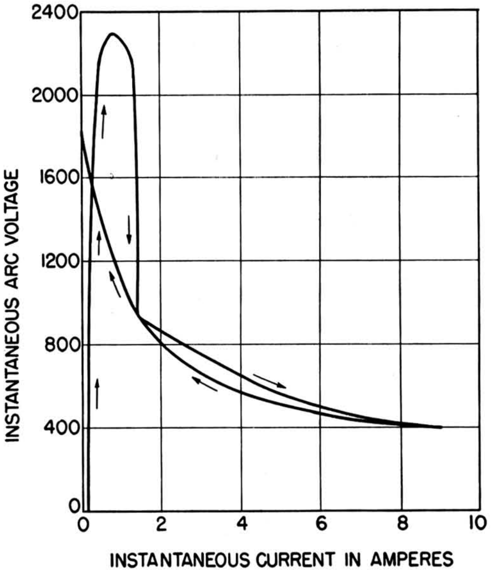

FIG. 4. Volt-ampere cyclogram of 60-cycle arc in hydrogen between copper electrodes 1.5 in. apart.

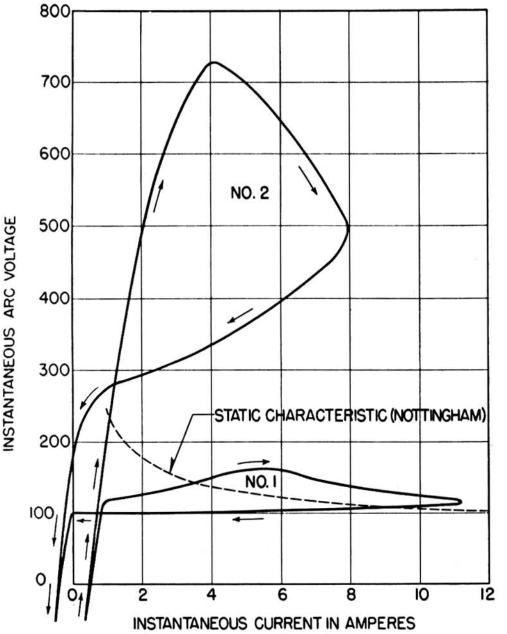

FIG. 5. Volt-ampere cyclograms of 60-cycle arcs in air between copper electrodes 1.5 in. apart. No. 1, arc still about 1.5 in. long; No. 2, arc lengthened by convection almost to breaking point.

hump appears to indicate re-ignition of the arc to a special low-current form which changes to the form normal for higher currents at 1.5 amp. With falling current the arc voltage follows the high-current characteristic right up to current zero. The dynamic volt-ampere characteristic of a similar arc in *air* is shown in Fig. 5. "No. 1" is for an early half-cycle and "No. 2" is for a half-cycle where the arc had been lengthened by convection almost to the breaking point in a 915-volt reactive circuit. The reversal of the loops near 1 amp in these figures is thought to be due to phase errors in the measuring devices.

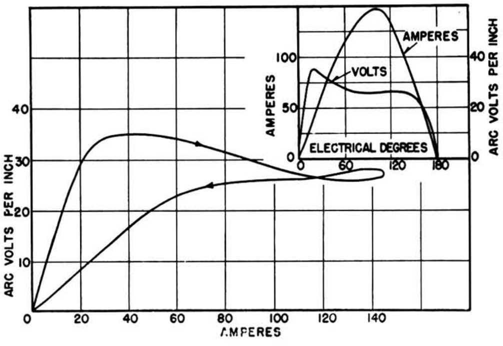

FIG. 6. Volt-ampere cyclogram of vertical 60-cycle arc 48 in. long in air, 100 amp rms.

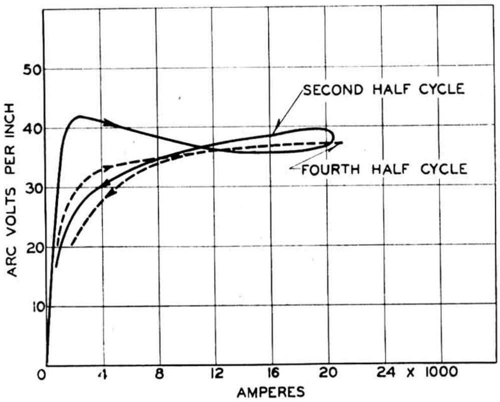

FIG. 7. Volt-ampere cyclograms of vertical 60-cycle arc 12 in. long in air, 15,000 amp rms.

It is evident that 60 cycles is not far from the natural frequency of response of these arcs in still air. The static characteristic shown dotted for comparison is the same as that plotted in Fig. 1.

At 100 amp rms, Fig. 6, taken from a paper by Strom (7), shows a rather similar cyclogram for a 48-in. long vertical 60-cycle arc in air. The time records of current and voltage gradient are shown in the inset. Fig. 7 shows the dynamic characteristics followed in two particular half-cycles by a similar arc 12 in. long carrying 15,000 amp rms. At this high current the upward trend of the arc voltage with current in the 5,000–20,000 amp range is clearly evident. It is believed that the nearly retraced dynamic characteristic should be approximated by equation [8]. On this assumption, the constant B lies between 26 and 38 volts/in.

Fig. 8 shows a cathode-ray volt-ampere cyclo-

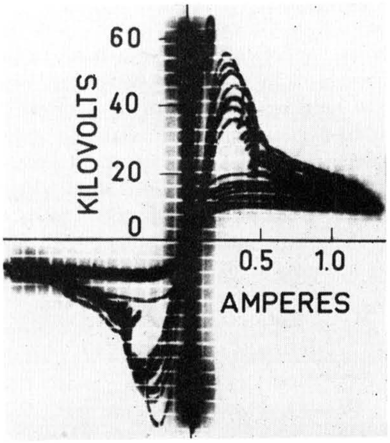

FIG. 8. Cathode-ray volt-ampere cyclogram of vertical 60-cycle arc drawn to a length of 48 in. in a 40-kv circuit in air.

gram of the extinction after somewhat more than one second of a 60-cycle magnetizing current (1.5 amp rms) arc drawn vertically to 48 in. length in a 40 kv circuit. At such a low current the static characteristic should follow the simple hyperbolic equation [6]. The rising (outer) portions of these traces at each polarity do tend to approach rectangular hyperbolas given by $D = 300$ watts/in. in equation [6]. The maintenance requirement for these arcs could be similarly expressed in terms of rms open-circuit volts times short-circuit current as 600 volt-amp/in.

This brief review of a few actual examples of dynamic a-c arc characteristics has shown not only the nature of these characteristics for plain-break arcs carrying 60-cycle currents from 1.5 to 15,000 amp, but also some approximate values applicable to *static* arc characteristic equations over this current range. The above data pertaining to the static open air arc characteristic may be roughly summarized by an equation similar to Ayrton's (3) but neglecting the C term:

$$V_a = 30\,(1 + L) + \frac{300\,L}{I}\ \text{volts} \qquad [12]$$

where L is in inches and I in amperes. In using any such equation, however, it must be kept in mind that actual arc voltages are so sensitive to particular conditions that departures from the equation by 100% or more are to be expected. As for the dynamic response of such arcs, it has been shown that they exhibit a great deal of hysteresis with 60-cycle alternating current, indicating that their "natural" response frequency is generally not far above 60 cycles. In hydrogen gas the normal arc form was shown to have a natural response frequency much higher than 60 cycles, but the hydrogen arc may also exist in a different low-current form which appears to have a much lower natural frequency. Very short arcs in which the electrode drops predominate may be expected to have much higher natural frequencies than the relatively long arcs used here as examples. The natural frequency of long arcs can be greatly increased by subjecting them to gas blasts or strong magnetic fields, or by forcing them into intimate contact with cool insulating surfaces.

MATHEMATICAL REPRESENTATION OF DYNAMIC ARC BEHAVIOR

Arc Column

So important are the transient or dynamic properties of arcs in electric circuits that it is worthwhile to try to express these properties mathematically so that they may be included in circuit equations. Since the electrode regions behave very differently from the column of an arc, the two regions must be considered separately. The following discussion will be limited to the dynamics of the arc *column*.

Development of dynamic arc equations.—The basic assumption upon which mathematical "models" of the arc column are based is that the column conductance per unit length $1/R = I/E$ can be expressed as a prescribed function of the additional stored energy per unit length (often called heat content), Q, associated with the conducting state of the arc column, or

$$\frac{1}{R} = F(Q) = F\left[\int (W - N)\,dt\right] \text{mho}, \qquad [13]$$

where R = column resistance per unit length, Q = excess energy content per unit length, W = electrical power input, watts per unit length, N = rate of energy loss, watts per unit length, and t = time.

In differential form, this equation is

$$\frac{d}{dt}\left(\frac{1}{R}\right) = (W - N)\,\frac{\partial F(Q)}{\partial Q} \qquad [14]$$

Particular arc model equations depend upon the forms assumed for $F(Q)$ and N. Two workable models have been proposed, each applicable especially to different limiting cases.

Mayr's equation.—The equation proposed and used by Mayr (8, 9) assumes

$$F(Q) = K \exp\,(Q/Q_o) \qquad [15]$$

and

$$N = N_o \qquad [16]$$

where K is an unspecified constant, Q_o is a constant energy quantity, and N_o is a constant rate of energy loss, all per unit length of the column. Since in the steady state

$$N = W = EI \qquad [17]$$

(E is the column voltage *gradient*), relation [16] defines an arc column with the static characteristic

$$EI = N_o \qquad [18]$$

or

$$V_aI = N_oL \qquad [19]$$

which is the same as equation [6] if N_o is identified with the constant D. Thus from the static viewpoint this model is best adapted to the low-current range of arc behavior, a range which is important when considering the *extinction* of high-power arcs. The quantity Q_o is defined by relation [15] as that energy quantity, the loss or gain of which is accompanied by a change in the arc column conductance by the factor ϵ (2.718). This quantity, Q_o, combined with the rate of energy loss, N_o, determines the characteristic response frequency, f_o, of the arc, or inversely the arc's *time constant*, which may be given the symbol θ and conveniently defined by the relation

$$\theta = Q_o/N_o \qquad [20]$$

Substitution of these three relations in the general equation [14] yields Mayr's arc model differential equation

$$R\frac{d}{dt}\left(\frac{1}{R}\right) = \frac{1}{\theta}\left(\frac{W}{N_o} - 1\right) \qquad [21]$$

If W is expressed as I^2R, this becomes

$$\frac{d}{dt}\left(\frac{1}{R}\right) + \frac{1}{\theta}\left(\frac{1}{R}\right) = \frac{I^2}{\theta N_o} \qquad [22]$$

which is a linear first order equation if the current $I = I(t)$ is determined solely by the connected circuit. If, on the other hand, W is written as E^2/R, where E is the column voltage gradient, equation [21] becomes

$$\frac{dR}{dt} - \frac{R}{\theta} = -\frac{E^2}{\theta N_o} \qquad [23]$$

which is a linear first order equation in R if the arc column gradient $E = E(t)$, is determined by the connected circuit alone. These equations have been used by Mayr to illustrate the behavior of arcs under a variety of interesting circuit conditions.

Cassie's equation.—A second arc model (10) assumes a column conductance simply proportional to Q, expressible by the relation

$$\frac{1}{R} = \frac{Q}{\theta E_o^2} \qquad [24]$$

and a power loss per unit length also proportional to Q according to

$$N = Q/\theta \qquad [25]$$

where E_o is a characteristic voltage gradient. Substituting these relations in the basic equation [14] yields Cassie's differential equation which can be written

$$R\frac{d}{dt}\left(\frac{1}{R}\right) = \frac{1}{\theta}\left[\left(\frac{E}{E_o}\right)^2 - 1\right] \qquad [26]$$

For this equation, the steady-state condition giving the static arc characteristic is

$$E = E_o \qquad [27]$$

or

$$V_a = E_oL \qquad [28]$$

which is the same as equation [8] for a high current arc if E_o is identified with the constant B. Cassie's equation, then, is most suitable for representing the arc column when its current is relatively large.

As before, linear first order equations may be obtained from [26] for cases where the circuit is an "infinitely stiff" source of either current or voltage. For impressed *current*, the equation can be written more conveniently

$$\frac{d}{dt}\left(\frac{1}{R^2}\right) + \frac{2}{\theta}\left(\frac{1}{R^2}\right) = \frac{2}{\theta}\left(\frac{I}{E_o}\right)^2 \qquad [29]$$

which is linear in $1/R^2$. For impressed *voltage*, the equation may also be slightly simplified to

$$\frac{dR}{dt} = \frac{R}{\theta}\left(1 - \frac{E^2}{E_o^2}\right) \qquad [30]$$

which is linear in R.

Uses of arc equations:

Applied voltage.—Simpler uses of the arc models involve only the easily solved linear differential equations [22], [23], [29], and [30]. For E constant, equation [30] can be readily integrated to

$$R = R_o \exp\left[\left(1 - \frac{E^2}{E_o^2}\right)\frac{t}{\theta}\right] \qquad [31]$$

where R_o is the value of R at $t = 0$. This shows that Cassie's model, like the actual arc, is unstable in a circuit which impresses a fixed voltage gradient, E, since any sustained nonzero value of the exponent will cause the exponential eventually to approach either zero or infinity, for which values the arc is either a short circuit or an open circuit. A similar inspection of the other equations shows that for either model a fixed *voltage* causes instability while conversely a fixed *current* always leads to stable operation. The same is true in general for any forms of rigidly impressed voltage or current varying only with time. For the special case of zero applied voltage Cassie's and Mayr's models both give the same result

$$R = R_o \exp (t/\theta) \qquad [32]$$

showing an arc resistance approaching infinity exponentially with the time constant θ. There is always some critical magnitude of any arbitrarily applied voltage gradient above which the resistance approaches zero instead of infinity. This critical gradient may be considered a breakdown value. Mayr (8) has worked out critical breakdown values and the behavior of arc resistance in terms of the constants of his arc model for various forms of applied voltage as functions of time. These results are significant particularly for the study of extinction or reignition just after current zero of a long a-c arc. The author (11) has extended this study by combining Mayr's model for impressed voltage in the period after current zero with Cassie's model for a large impressed current during the conducting period prior to current zero. The behavior of this composite model can be expressed in terms of the amplitude and frequency of the prior current as well as the arc conditions, θ and E_o, and the form of the restored voltage.

Applied current.—A solution of Mayr's equation [21] for impressed current which is of special interest is that for a sine-wave alternating current $I = I_1 \sin \omega t$, giving the dynamic characteristic of an a-c arc in a reactive circuit with generated voltage much larger than the arc voltage. This is the usual case for arcs in circuit breakers interrupting a-c short circuits.

For the cyclic steady state (each successive cycle the same) Mayr gives a solution for the arc voltage gradient which leads to

$$E = \frac{2E_1 \sin \omega t}{\left[1 - \frac{\sin(2\omega t + \varphi)}{\sqrt{1 + (2\omega\theta)^2}}\right]} \quad [33]$$

where

$$\varphi = \cot^{-1}(2\omega\theta) \quad [34]$$

and

$$E_1 = N_o/I_1 \quad [35]$$

is the voltage gradient on the static arc characteristic at the peak current, I_1. For 60-cycle arcs E_1 is very nearly the actual arc gradient at and near the current peak where dI/dt is near zero. Fig. 9 shows a number of a-c volt-ampere cyclograms plotted according to equation [33] for several values of the product $\omega\theta$, which expresses the relation between the frequency of the current and the natural frequency of response of the model arc column. The general resemblance of some of these curves to the oscillographic traces in Fig. 8 is evident.

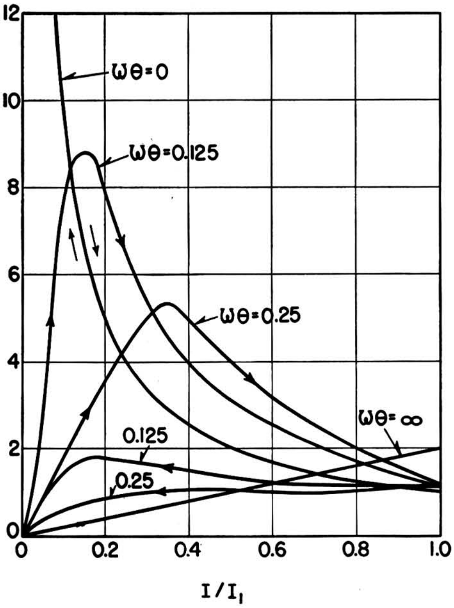

FIG. 9. Dynamic a-c arc characteristics computed by O. Mayr (8) from his arc equation. θ = Arc time constant; ω = angular frequency of arc current; $I = I_1 \sin \omega t$.

A mathematically simple treatment of the arc model behavior near current zero for an a-c arc will be demonstrated for Cassie's model. For the region near current zero where $\omega \ll \pi/2$ the sine wave of current is given with sufficient accuracy by the simple linear expression,

$$I = I_1\omega t \quad [36]$$

which, when substituted in equation [22], gives an expression for the arc resistance. When multiplied by the current this gives the arc voltage gradient in terms of time for the cyclic steady state,

$$E = \sqrt{2}\, E_o \frac{t/\theta}{\sqrt{1 - t/\theta + 2(t/\theta)^2}} \quad [37]$$

Fig. 10 shows a plot in dimensionless coordinates of this equation with the negative time portion superimposed on that for positive time to simulate a volt-ampere cyclogram for one half-cycle. As shown, the linear current variation permits interpreting the abscissa units as either t/θ or $I/I_1\omega\theta$, as related through equation [36]. The general resemblance between these curves and the oscillographic records for the long 60-cycle arcs in Fig. 6 and 7 indicate the suitability of Cassie's arc model equation for approximating the dynamic behavior of arcs carrying power-frequency currents of hundreds or thousands of amperes.

By comparing actual dynamic arc characteristics with plots for the appropriate models, one can estimate values of the time constant θ for these arcs. For example, the re-ignition voltage peak occurs in the Cassie model plot, Fig. 10, at $I = I_1\omega\theta$; so $\omega\theta$ should be given by the value of I/I_1 at the ob-

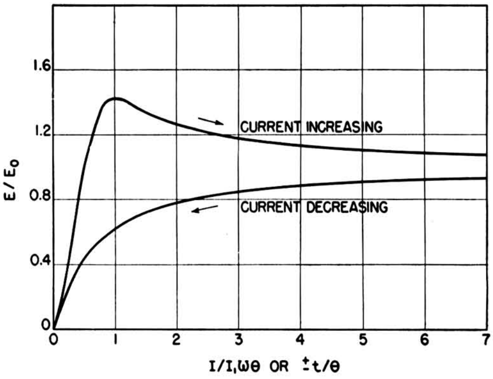

FIG. 10. Dynamic a-c arc characteristic near current zero. Computed from A. M. Cassie's arc equation for higher current arcs. θ = Arc time constant; current: $I = I_1\ \omega t$.

served voltage peak for any a-c arc behaving according to Cassie's equation. The estimates of θ by this means for the 60-cycle arcs of Fig. 6 and 7 are about 800 and 300 μsec, respectively, for the second half-cycle. If the curves in Fig. 8 are judged to correspond most nearly to a curve for $\omega\theta = 0.2$ in Fig. 9, the indicated value in Mayr's model for the 1.5 amp arc of Fig. 8 would be about 500 μsec. The fact that these estimated values are all of the same order tends to support a basic assumption underlying the use of these models that θ is a characteristic arc constant not primarily dependent on the current magnitude. In treating the case of a small amplitude current oscillation superimposed on a constant arc current, Mayr shows that the natural response frequency of a model arc column may logically be defined as the frequency for which $\omega\theta = 1$. From this,

$$f_o = \frac{1}{2\pi\theta} \qquad [38]$$

giving indicated values of about 200, 500, and 300 cycles/sec, respectively, for the arcs of Fig. 6, 7, and 8.

Interaction of arc with circuit.—Unfortunately, the arc model equations [21] and [26] without restrictions on interaction with the connected circuit are nonlinear and so not amenable to straightforward general solutions. Mayr, however, has shown a graphical method (9) for getting approximate solutions showing the behavior of his arc model in a simple circuit with capacitance directly in parallel with the arc and resistance limiting the current from a constant potential source. The circuit is that of Fig. 3 with all values zero except R_s and C. In general, the graphical solutions gave spirals on the voltage-current diagram either converging to or diverging from a point on the static arc characteristic corresponding to the point A in Fig. 1 for a stable arc in a purely resistive circuit. More or less similar spirals often are observed in actual volt-ampere oscillograms of long arcs re-igniting after a current zero, as for example in Fig. 8.

Another useful approximate method for dealing with the nonlinear arc model equations is that of small variations. For combination with circuit equations it is convenient to express arc resistance or conductance in terms of the current and voltage gradient, giving for Mayr's equation [21]:

$$\frac{1}{I}\frac{dI}{dt} - \frac{1}{E}\frac{dE}{dt} = \frac{1}{\theta}\left(\frac{EI}{N_o} - 1\right) \qquad [39]$$

If $I = I_1 + i$ and $E = E_1 + e$, where I_1 and E_1 are constant values on the static characteristic with $E_1 I_1 = N_o$, $i \ll I_1$, and $e \ll E_1$, neglect of minor terms gives the linear first order equation in two unknowns,

$$E_1\frac{di}{dt} - I_1\frac{de}{dt} = \frac{E_1 i + I_1 e}{\theta} \qquad (40)$$

which can be solved in combination with linear equations of the connected circuit by converting the gradients to total voltages for a constant arc length, L. Although these solutions are valid only for small excursions from the steady state, they are useful for investigating *stability* conditions. It is interesting to note that equation [40] for small deviations only can be obtained from Cassie's equation [26] as well as from Mayr's equation [21] if E_1 is taken equal to E_o.

Mayr has shown (8) the mathematical details of these solutions for a number of simple circuit arrangements. One result of great simplicity and also of special interest was obtained for a circuit with capacitance directly in parallel with the arc. The special limitation is that the source resistance or inductance is so high that the total current to the arc and its shunting capacitance is held constant or permitted to change only at a rate small compared with possible rates of variation in arc current. If the steady-state arc resistance (total) is

$$R_s = \frac{E_1 L}{I_1} \qquad [41]$$

the limiting condition for arc stability proves to be simply

$$R_s C = \theta \qquad [42]$$

or equality between the time constant of the arc and the time constant for discharge of the shunting capacitance through the arc's momentary resistance. For $R_s C < \theta$ any small departure from the steady state tends to disappear; for $R_s C > \theta$, such a departure tends to increase, leading to oscillations of increasing amplitude which may result in arc extinction. If the second inequality is great enough, arc extinction may occur in a simple exponential manner without oscillation.

From a physical viewpoint, one may say that in a circuit where the arc is stabilized by a large source impedance, the presence of capacitance in parallel with the arc may lead to instability if

$$C \geqslant \theta/R_s \qquad [43]$$

In terms of voltage and current, the instability condition is

$$I_1 \leqslant CV_a/\theta \qquad [44]$$

where $V_a = E_1 L = R_s I_1$. This shows that, for a circuit-controlled current approaching zero, some limiting value will be reached at which the residual capacitance shunting the arc terminals will cause instability, and the arc will "go out" before the actual current zero is reached. This is a common situation with a-c arcs in highly inductive (low power factor) circuits. When arc failure just before a normal current zero occurs at the instantaneous current I_1 in equation [44], the current is diverted into the shunting capacitance, which generally includes the equivalent parallel capacitance associated with the current limiting impedance. The current diversion will occur in a time of the order of θ, which is often so short on the time scale of the normal or circuit-impedance-limited current fall that the diversion may be considered instantaneous. In this case, most of the stored energy associated with the arc failure current I_1 in the circuit inductance must reappear in the shunting capacitance, which will be charged to a peak voltage given approximately by

$$V_p = I_1\sqrt{L/C} \qquad [45]$$

Substituting for I_1 from equation [44]

$$V_p = V_a\sqrt{LC}/\theta \qquad [46]$$

showing that the voltage "surge" resulting from arc failure, often called "current chopping," increases with the arc voltage, with the reciprocal of the arc time constant, and also with the product of the circuit inductance *times the shunting capacitance.* This shows the basis for a fact often observed (12) but not always fully appreciated, that the addition of shunting capacitance may actually *accentuate* rather than suppress overvoltage surges resulting from current chopping by a-c arcs.

Electrode regions.—Conditions at anode and cathode terminals of an arc are so incompletely understood that dynamic equations for the voltage drops in these regions are not generally attempted, although it does appear that part of the hysteresis effects in the voltage of relatively short arcs does reside in these regions.

Emanating from both the anode and the cathode of high-current arcs are high-velocity vapor blasts which may markedly affect conditions in the arc column as well as the anode and cathode voltage drops. The effective time constant θ of the cathode drop for a thermionic cathode, which is the normal type when refractory cathode materials like carbon or tungsten are used, might be expected to be much greater than for a so-called "cold" cathode existing on low-boiling metals. The voltage drops at the latter type of cathode and at the anode appear to depend on phenomena taking place in such extremely thin layers of gas at the electrode surfaces that their thermal or electrical inertia is necessarily exceedingly small—very much less than the smallest values of θ observed for arc *columns.* This is true even for those columns existing in intense gas blasts. That very short time constants are characteristic of these electrode regions is illustrated by sudden jumps in arc voltage often observed near current zero and attributable to transitions between the *arc* cathode with around 10 volts drop and the *glow* cathode with a few hundred volts drop. These short electrode-region time constants help explain, with the aid of equation [44], the relative instability of short metal-electrode arcs. The stabilizing effect of carbon or tungsten electrodes with their slow-responding thermionic cathode spots is similarly explainable.

Short a-c arcs between low-boiling metal electrodes are subject to a special kind of instability sometimes called the rectifying effect, resulting from the loss of the cathode spot when the current passes through zero and tries to reverse. In the absence of electrode temperatures high enough for copious thermionic emission, a new cathode spot must be formed by breakdown of a gaseous space charge layer requiring a few hundred volts minimum (13). Further increase in the required restriking voltage after a current zero results if the circuit natural frequency is such that a few tens or hundreds of microseconds delay occurs in the application of voltage. The rate of this recovery of dielectric strength with time after current zero has been found (14) to be higher for *shorter* electrode separations, for lower boiling temperatures of the electrode surfaces, and for lower 60-cycle current magnitudes.

CONCLUSION

The foregoing discussion of electrical characteristics of arcs, both static and dynamic, has emphasized features believed to be most significant in present-day applications. Some mathematical techniques applicable to calculation of transient conditions in circuits including electric arcs have been outlined. It should be recognized that actual arc behavior is generally so sensitive to small variations in conditions and so incompletely understood in detail that only very approximate calculations can be justified. Nevertheless, it is hoped that this presentation may be of some use as a starting point in attempts by engineers to understand and analyze approximately the behavior of circuits and devices involving arcs.

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

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Diffusion of Cobalt in Molybdenum[1]

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ABSTRACT

Diffusion coefficients for cobalt in molybdenum were determined at 900°, 1100°, 1275°, 1500°, and 1700°C. In the equation relating diffusion coefficient with temperature, $D = Ae^{-Q/RT}$, the activation energy Q derived was 34,800 cal/mole, and the constant A was 2.82×10^{-6} cm²/sec.

Introduction

Diffusion coefficients for cobalt in molybdenum were determined in order to estimate minimum sintering times for complete homogenization for powder metallurgy applications. Ruder and Birchenall (1) report the self diffusion of cobalt as $D = 0.032 \exp(-61{,}900/RT)$ cm²/sec, and the diffusion of cobalt in nickel as $D = 1.46 \exp(-68{,}300/RT)$ cm²/sec, but no data were found for diffusion of cobalt in molybdenum.

A small solid solution concentration range is involved in this system, the maximum solubility of cobalt in molybdenum being around 3 wt % at 1620°C according to the phase diagram of Sykes and Graff (2), and decreasing to about half of one per cent at room temperature.

Theory

It can be shown theoretically that the rate of advance of a zone of concentration is a simple function of the diffusion coefficient, and for linear diffusion, Barrer (3) states the rate is likely to be governed by the equation

$$W^n = 4\,Dt \qquad \text{(I)}$$

where W denotes the distance of discontinuity from the origin, D is the diffusion coefficient, t is the time, and $n = 2$.

The theoretical work of Fick was published in 1855 and is still regarded as the descriptive basis of diffusion theory. The diffusion at 1500° and 1700°C was determined by the method outlined by Rhines and Mehl (4) of analyzing chemically the chips machined at increments from the interface and applying Matano's solution of Fick's law,

$$\frac{\partial c}{\partial t} = \frac{\partial}{x}\left(D\,\frac{\partial c}{\partial x}\right) \qquad \text{(II)}$$

which provides for the possibility of a variation of D with concentration c. For constant time t, Rhines and Mehl simplify equation (II) to,

$$D = \frac{1}{2t}\,\frac{dx}{dc}\int_o^c x\,dc \qquad \text{(III)}$$

and this equation was used to solve graphically for D, where dx/dc is the slope of the penetration curve at concentration c, and $\int_o^c x\,dc$ is the area enclosed by the curve, the interface, and the limits of concentration O and C. The interface used in defining the area $\int_o^c x\,dc$ is not the original interface, but is defined as the surface through which an equal number of the two kinds of atoms have passed in opposite directions. In using equation (III), the diffusion is considered planar rather than radial.

The universally accepted form of the equation relating D with temperature is,

$$D = Ae^{-Q/RT} \qquad \text{(IV)}$$

where D, the diffusion coefficient, represents the atomic mobility, and Q, the activation energy, is a measure of the potential barrier that surrounds a diffusing atom. A is a constant, T the absolute temperature, and R the gas constant. In logarithmic form the equation is,

$$\log_e D = \log_e A - Q/RT \qquad \text{(V)}$$

and when the natural logarithm of D is plotted against the reciprocal of the absolute temperature, the slope is Q/R.

Procedure

900°, 1100°, and 1275°C Runs.—Cobalt-molybdenum couples were prepared by inserting a rod of cobalt into a hollow cylinder of molybdenum and closing the opening with a molybdenum plug. The cobalt inner rod was 0.250 in. in diameter by 1 in. long. The outer cylinder, 0.250 in. I.D. by ⅝ in. O.D. by 2 in. long, was made from swaged molybdenum rod.

The couples were placed upright in a furnace at room temperature, heated to temperature, and held

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[2] Present address: Sylvania Electric Products Inc., Towanda, Pa.

for different times in a hydrogen atmosphere. After cooling to room temperature, the specimens were cut at midsection for metallographic examination.

After etching with a solution of 4 parts to 1 by volume of 30% H_2O_2 and 85% H_3PO_4, the widths of the Co-Mo phase were measured directly on the specimens with a Gaertner comparator. Widths were determined also by measuring with a vernier to 0.001 in. on a ground glass screen at 1000× projection, and again by scaling from photomicrographs made at 500× magnification. Neither of the latter two methods appeared to be as reliable as direct measurement with the comparator.

1500° and 1700°C Runs.—The couples for these runs consisted of an inner rod of an alloy of molybdenum and 3.42% cobalt, prepared by powder metallurgy technique, and an outer cylinder of molybdenum with molybdenum plugs at each end. The alloy of 3.42% cobalt was chosen in preference to pure cobalt to eliminate the possibility of melting, and to have a single-phase system. The inner cylinder was 0.375 in. in diameter by 2-¾ in. long; and the outer cylinder was 0.375 in. I.D. by ⅝ in. O.D. by 3-¾ in. long. The couples were heated for 95 hr at temperature in a hydrogen atmosphere in a refractory lined furnace and then removed for machining of 0.010 in. diameter cuts.

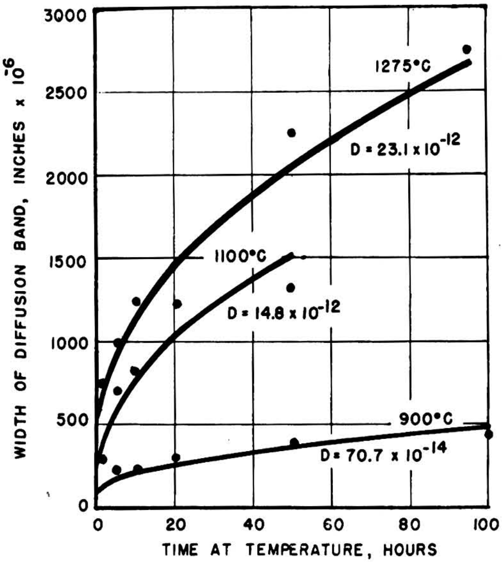

FIG. 1. Width of diffusion band of Co-Mo phase

TABLE I. *Width of diffusion band of single-phase* Co-Mo *for 900°, 1100°, and 1275°C determinations*

Diffusion temp, °C	Experimental data: Time at temp, hr (A)	Experimental data: Width* of diffusion band, in. × 10^{-6} (B)	Data using first measured width as starting point: Time, hr (C)	Data using first measured width as starting point: Width in. × 10^{-6} (D)	Calculated D using data of (C) and (D) and equation $W^2 = 4 \cdot D \cdot T$ (cm²/ sec) (E)
900	0	96†	—	—	—
	1	136	4	92	94.8×10^{-14}
	5	228	9	120	71.7×10^{-14}
	10	256	19	183	79.0×10^{-14}
	20	319	49	266	64.7×10^{-14}
	50	402	99	309	43.2×10^{-14}
	100	445	—	—	Avg 70.7×10^{-14}
1100	0	227†	—	—	—
	1	318	4	392	17.2×10^{-12}
	5	710	9	513	13.1×10^{-12}
	10	831	19	922	20.0×10^{-12}
	20	1240	49	987	8.9×10^{-12}
	50	1305	—	—	Avg 14.8×10^{-12}
1275	0	465†	—	—	—
	0.5	563	0.5	187	31.3×10^{-12}
	1	750	4.5	437	19.0×10^{-12}
	5	1000	9.5	687	22.3×10^{-12}
	10	1250	19.5	875	17.6×10^{-12}
	20	1438	49.5	1687	25.8×10^{-12}
	50	2250	94.5	2187	22.7×10^{-12}
	95	2750	—	—	Avg 23.1×10^{-12}

* Measured on specimen with comparator to 10^{-3} MM.

† Calculated width for time furnace and specimen is coming up to temperature.

DISCUSSION OF EXPERIMENTAL DATA

The widths of the phase Co-Mo in the 900°, 1100°, and 1275°C runs are listed in Table I and plotted in Fig. 1. Analysis of the data by the method of least squares gave values of $n = 2.47, 2.22$, and 2.07. Using the accepted value of 2 for n, values of D were computed from the widths of the diffusion band. Photo-

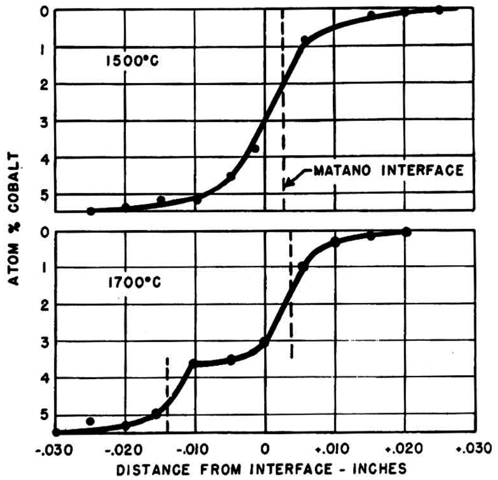

FIG. 2. Concentration-distance curves

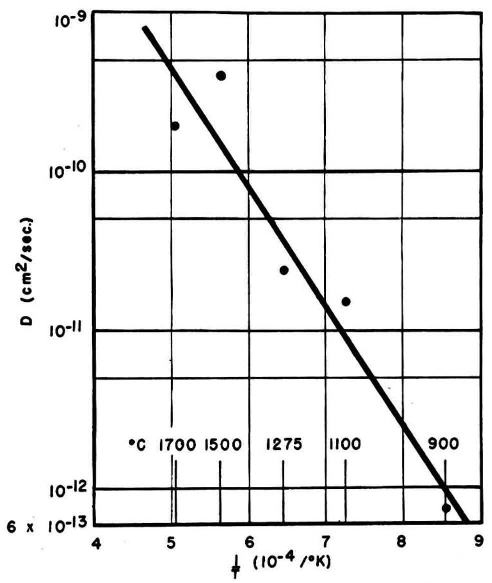

FIG. 3. Temperature dependence of diffusion coefficient

micrographs of the 1- and 50-hr specimens at 900°C are typical of the appearance at the interface and are reproduced in Fig. 4 and 5 at 500× magnification.

The *c-x* data for the 1500° and 1700°C runs are listed in Table II and plotted in Fig. 2. The concentration ratio-distance data are also listed in Table II. When the latter data were plotted on prob-

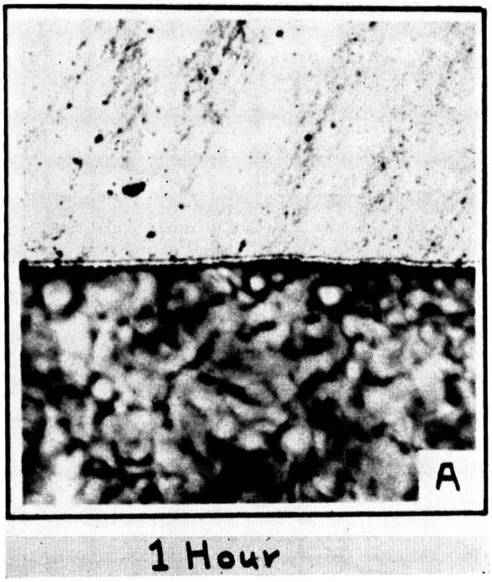

FIG. 4. Co-Mo band after 1 hr at 900°C. Magnification, 500×. Etch, 4:1 H_2O_2:H_3PO_4.

TABLE II. *Concentration—distance data for 1500° and 1700°C determinations*

Temp, °C	Range of diameter of cut, in.	Distance from interface, in.	Cobalt		$\frac{C - C_0}{C_1 - C_0}$*
			Wt %	Atom %	
1500	0.430–.420	+0.025	0.010	0.016	0.0029
	0.420–.410	+0.020	0.022	0.036	0.0066
	0.410–.400	+0.015	0.091	0.148	0.0272
	0.400–.375	+0.0063	0.546	0.890	0.163
	0.375–.370	−0.0013	2.37	3.81	0.700
	0.370–.360	−0.005	2.81	4.50	0.825
	0.360–.350	−0.010	3.24	5.17	0.948
	0.350–.340	−0.015	3.23	5.15	0.944
	0.340–.330	−0.020	3.40	5.42	0.995
	0.330–.320	−0.025	3.41	5.44	0.997
	0.320–.310	−0.030	3.42	5.45	1.000
1700	0.430–.420	+0.025	0.003	0.005	0.00092
	0.420–.410	+0.020	0.003	0.005	0.00092
	0.410–.400	+0.015	0.014	0.123	0.0226
	0.400–.390	+0.010	0.111	0.181	0.0332
	0.390–.380	+0.005	0.602	0.978	0.179
	0.380–.370	Interface	1.90	3.03	0.556
	0.370–.360	−0.005	2.18	3.51	0.644
	0.360–.350	−0.010	2.20	3.54	0.650
	0.350–.340	−0.015	3.16	5.05	0.926
	0.340–.330	−0.020	3.26	5.19	0.953
	0.330–.320	−0.025	3.24	5.17	0.949
	0.320–.310	−0.030	3.42	5.45	1.000

* C = Cobalt concentration at distance from interface.
C_0 = Minimum cobalt concentration.
C_1 = Maximum cobalt concentration.

TABLE III. *Derived diffusion coefficients from 1500° and 1700°C runs*

Temp, °C	Cobalt			D cm²/sec
	Atom %	Wt %		
1500	0.1	0.062		3.53×10^{-10}
	0.5	0.300		6.17×10^{-10}
	1.0	0.650		3.53×10^{-10}
	2.0	1.25		3.94×10^{-10}
	3.0	1.90		4.30×10^{-10}
	4.0	2.50		3.60×10^{-10}
			Avg	4.18×10^{-10}
1700 (single phase)	0.1	0.062		2.80×10^{-10}
	0.5	0.300		2.85×10^{-10}
	1.0	0.650		1.27×10^{-10}
	2.5	1.55		1.39×10^{-10}
	3.0	1.90		1.75×10^{-10}
	3.5	2.20		1.50×10^{-10}
			Avg	1.93×10^{-10}
1700 (two phase)	4.0	2.50		0.47×10^{-10}
	4.5	2.80		1.39×10^{-10}
	5.0	3.15		5.57×10^{-10}

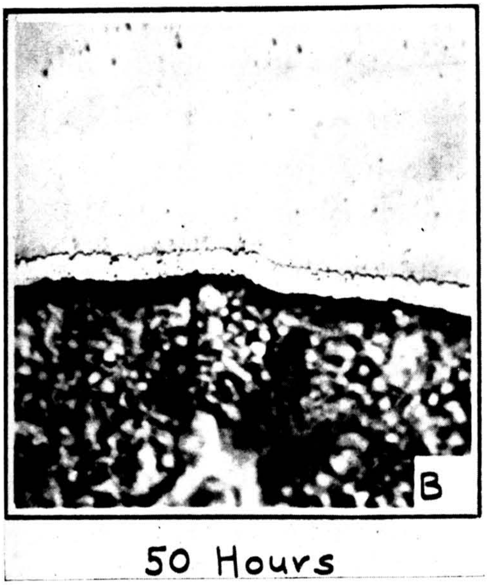

FIG. 5. Co-Mo band after 50 hr at 900°C. Magnification, 500×. Etch, 4: 1 H_2O_2:H_2PO_4.

ability paper, either a slightly curved line or a straight line fitted the 1500°C run. The points all fell on a curved line for the 1700°C run. DaSilva and Mehl (5) point out that the plot on probability paper makes it much easier to draw a best fit to eliminate doubtful points. Wells (6) states a curved line indicates a variation of D with C and the Matano method of analysis should be used. The derived diffusion coefficients listed in Table III do not show a consistent variation of D with increasing cobalt but, as previously pointed out, a rather small range of concentration is considered.

The variation of D with temperature has been plotted in Fig. 3.

Values of Q and A were derived from the experimentally determined values of D from runs at the three lower temperatures. Q and A were based on these values of D because 21 specimens were used compared to the 2 specimens for the 1500° and 1700°C runs. It should be noted also that diffusion coefficients for the latter two temperatures appear to be of the correct order of magnitude, but are of inverse magnitude.

Analysis by the method of least squares of the values of D for all temperatures gives values of $Q = 36{,}400$ cal/mole and $A = 5.17 \times 10^{-6}$ cm^2/sec, but for the reasons given previously, the values of $Q = 34{,}800$ and $A = 2.82 \times 10^{-6}$ are deemed more likely correct.

SOURCES OF ERROR

Sources of error in the Matano method of analysis are discussed in considerable detail by Rhines and Mehl (4) and their paper should be read for discussion of the precision of this method. The largest source of error in the 1500° and 1700°C runs is probably in the machining of chips for chemical analysis because of brittleness of the metal at the interface. The inversion of the derived diffusion coefficients at these temperatures may be partly attributed to difficulties in operating at the higher temperatures.

ACKNOWLEDGMENT

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

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Corrosion of Titanium in Fused Chlorides

Formation of Pyrosols[1]

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ABSTRACT

Titanium was severely attacked when immersed in a molten alkali chloride bath in the presence of air. The most severe corrosion of this metal was observed in molten NaCl-NaF mixtures; samples disintegrated completely at temperatures of 850°C in less than 3 hr. Progressively less corrosion occurred in KCl, NaCl, and LiCl melts. In many cases, salt fumes were more corrosive than the molten salt itself, evidently because of the better access of oxygen to the titanium surface. The corrosion rate fluctuated greatly from test to test but was very low in experiments performed in vacuum.

The chief corrosion products were a dispersion of metallic titanium in the molten salt ("pyrosols"), mixed with some titanium oxides. The mixture was dark gray, and colored the solid salt bluish-black. White to yellowish oxides appeared in small amounts on the surface of the salt bath and consisted mainly of TiO_2.

INTRODUCTION

The high corrosion resistance of titanium is frequently emphasized. However, investigations have shown that titanium does not always exhibit excellent properties in this respect. For example, the metal is destroyed quickly by hydrofluoric acid (1), and is readily attacked by the great majority of other acids, strong and weak, if water soluble fluorides are present (2). No references could be found as to the resistance of titanium against the attack of fused salt baths at temperatures above 700°C. Such knowledge is of importance in studies of the electrolytic deposition of titanium from fused salt baths (3). If titanium corrodes to any great extent in fused electrolytes, the difficulty of titanium deposition would be partially explained. The purpose of the present investigation, therefore, was to establish the extent of corrosive attack of various salts on titanium at high temperatures in the presence of air and also in vacuum.

EXPERIMENTAL PROCEDURE

For this study, sodium chloride, potassium chloride, lithium chloride, and sodium fluoride were chosen because they are frequently used for electrolytes. The first two were U.S.P. grade, granular.[2] The salts were melted in porcelain crucibles in a resistance furnace, the temperature of which was controlled by a variable transformer, and measured by a chromel-alumel thermocouple. Titanium samples were cut from cold rolled and annealed sheet 1.6 mm thick, of 97+ % purity (1).

Titanium samples were first weighed and measured with a micrometer, after which they were submerged in the molten salt bath, held at a constant temperature for the set length of time, and then cooled together with the salt. The salt was dissolved from the sample with hot water, and the samples then washed with cold water, weighed, and measured, so that the percentage loss in weight and the average rate of corrosion could be calculated.

It was found that the titanium samples must be placed in the salt after it is molten, rather than melt the salt with the sample in it; samples must be allowed to cool submerged in the bath, otherwise the metal oxidized at a fast rate during the heating and cooling period. It was necessary to suspend the titanium in the bath so that it would not come in contact with any part of the crucible. A hole was drilled in one end of the sample so that it could be supported either by a platinum wire, or pure iodide titanium hook, hanging from a quartz rod resting across the crucible top.

Tests were also made with only one end of the sample submerged in the molten sodium chloride, while the other end projected out of the crucible into the furnace atmosphere of hot salt fumes, to compare the attack at the two ends. A few tests were made by heating the titanium in air with no salt present.

Other tests were made by placing titanium samples with sodium chloride in a Vycor glass tube; the tube was evacuated, heated to drive off adsorbed moisture,

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[1] Manuscript received May 4, 1954. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954. Based on a portion of work carried out at the Missouri School of Mines and Metallurgy for the Wright Air Development Center under Contract No. AF 33(616)-75.

[2] LiCl was a purified material obtained from J. T. Baker Chemical Company, and the NaF was "Baker Analyzed" reagent.

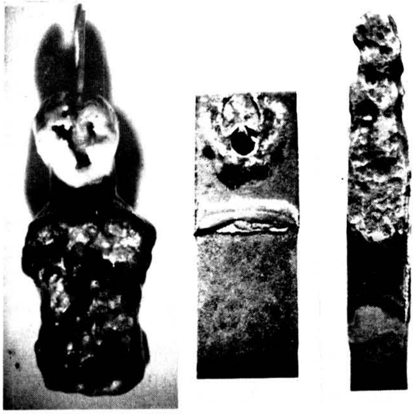

FIG. 1*a*. (Left) Ti sample removed from the molten NaCl bath where it corroded for 6 hr at 900°C, with corrosion products on its surface; FIG. 1*b*. (Center) a similar sample with corrosion products washed away; FIG. 1*c*. (Right) another sample, the end of which is pencilled by severe attack of NaCl fumes and oxygen (of the air).

and then sealed while still being evacuated. Samples in the sealed tube were heated in a resistance furnace.

EXPERIMENTAL RESULTS

Attack by sodium chloride.—Titanium samples were strongly attacked by the molten sodium chloride in the presence of air. Fig. 1*a* shows a sample that was partially immersed, then withdrawn from the molten bath and allowed to cool quickly. The part submerged in the bath was covered with a thick layer of a black material, adhering to the metal, while the part above the liquid salt exposed only to the salt fumes was covered with a white residue. After the corrosion products were washed off with water, the reduction in size of that part of the sample that was immersed in the bath was very evident (Fig. 1*b*). In every instance the titanium metal that had been in the corrosive medium was surrounded by a blue-black deposit, which was most dense immediately around the titanium, as seen in Fig. 2, which shows a section through the metal and salt, after they had been cooled slowly in the furnace. Upon dissolving the salt in water, a fine, dark gray powder was collected for identification. The powder dissolved readily in hydrofluoric acid with hydrogen evolution, except for a small residue that proved to be titanium oxide, thus revealing the metallic nature of the corrosion product. X-ray diffraction patterns showed that the powder had a slightly expanded metallic titanium lattice. This demonstrates that solid titanium samples were partially dispersed in molten salt, in the form of a metallic fog or a "pyrosol," according to Lorenz (4). Formation of a metallic fog in the cathodic compartment during the electrolysis of fused salts is a well-known phenomenon. X-ray analysis showed further that the white material on the upper part of the titanium sample contained some titanium dioxide in the form of rutile. The other constituents of the white deposit have not yet been identified. Corrosion of the titanium samples by sodium chloride melts, resulting in pyrosol formation, was heavy and very irregular; the results obtained fluctuated greatly (see Table I). However, in the absence of air (in vacuum) corrosion was much less. Titanium gained in weight if heated in air in the absence of salt, evidently because of the adsorption of oxygen and the formation of an oxide coating. These coatings had a yellowish appearance.

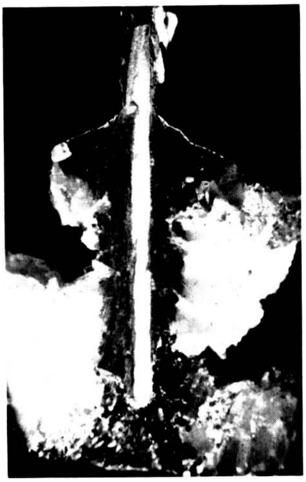

FIG. 2. Cross section through the Ti sample and NaCl, in which the metal corroded for 2 hr at 900°C. Dark corrosion products surround the Ti.

TABLE I. *Loss due to corrosion of titanium samples in molten* NaCl *at 850°C, in 3 hr*

Sample No.	Initial wt, g	Final wt, g	Loss in wt, %	Condition of Ti samples
5	0.3160	0.2022	36.0	Suspended by Pt wire
6	0.3986	0.2142	46.3	Suspended by Pt wire
7	0.6735	0.5489	18.5	Suspended by Ti wire
8	1.3270	0.9476	28.6	Half in and half out of NaCl
10	1.0606	0.9824	7.4	Half in and half out of NaCl
9a	0.8459	0.8574	1.36 gain	Heated alone in air
10a	0.8898	0.9157	2.91 gain	Heated alone in air
11	0.6417	0.6374	0.67	In NaCl in vacuum
12	0.5633	0.5535	1.74	In NaCl in vacuum
12a	0.5720	0.5672	0.84	In NaCl in vacuum

Since the greatest loss in weight was exhibited by samples suspended from a platinum wire, it was thought that this corrosion process might also be electrochemical in nature, accelerated by the

TABLE II. *Corrosion rates of titanium samples in molten* KCl, LiCl, *and* KCl-LiCl *mixtures*

Sample No.	Bath	Temp, °C	Time, hr	Wt loss, %	Corros. rate, mg/cm^2 hr	Conditions of Ti samples
14A	KCl	800	3	3.4	3.1	Susp. by Ti wire
18A	KCl	850	3	24.0	19.5	Susp. by Ti wire
18B	KCl	850	3	9.5	7.1	Susp. by Ti wire
19A	KCl	850	3	78.6	50.2*	Half in, half out of KCl
19B	KCl	850	3	88.0	53.5*	Half in, half out of KCl
26A	KCl	850	1	12.4	21.0*	Half in, half out of KCl
26B	KCl	850	2	27.8	25.4*	Half in, half out of KCl
26C	KCl	850	3	60.7	35.0*	Half in, half out of KCl
31	KCl	850	4	2.8	1.38	Vacuum, half out of KCl
32	KCl	850	6	4.3	1.42	Vacuum, half out of KCl
14B	LiCl	625	3	3.2	2.9	Susp. by Ti wire
15	LiCl	625	3	2.3	2.0	Susp. by Ti wire
25B	LiCl	850	3	6.9	4.84	Susp. by Ti wire
16	LiCl	625	3	3.3	2.5	Half in, half out of LiCl
20A	LiCl	850	3	35.8	19.5	Half in, half out of LiCl
20B	LiCl	850	3	20.6	13.7	Half in, half out of LiCl
17A	KCl+ LiCl	375	3	0.4	0.4	Susp. by Ti wire
17B		375	3	1.3	0.8	Half in, half out of LiCl

* Heavy or very heavy attack of the projecting end (Fig. 1c); in all other cases the submerged end was attacked more.

platinum which acted as a cathode. To check this possibility, a short piece of platinum wire was firmly connected to the bottom of a titanium sample, which was suspended on a titanium wire hook in molten sodium chloride for 3 hr. When the salt was washed away there was no evidence of a heavier attack at the point where the platinum wire was connected than on the sample as a whole. This experiment indicates that the heavy corrosion of sample No. 6 (Table I) was accidental and within the range of fluctuations (7–46%) exhibited by similar experiments. Although the parts of the titanium samples which were outside of the salt bath were usually not as heavily corroded as the ends immersed in the bath, in the case of sample 8 (Table I) there was the opposite result; the heavily attacked upper end of the sample is shown in Fig. 1c.

Attack by potassium chloride and lithium chloride.—In these experiments the rate of corrosion in mg/cm^2 hr was determined. The weight of the samples was beteeen 0.3 and 0.7 g with a surface area between 1.3–3 cm^2 exposed to the action of the salt bath. For those samples only half immersed in the bath, so as to study the influence of the hot salt fumes, the two ends were usually unevenly attacked; nevertheless the total loss was determined by weighing, and the rate of corrosion computed on the whole area of the sample. To study the influence of temperature, eutectic mixtures of potassium and lithium chlorides (40–60 mole %) with a melting point of 355°C were used. These mixtures approached in their composition those used in electrolysis of titanium by Cordner and Worner and others (3, 5, 6). Results of these corrosion experiments are summarized in Table II. Again, rates of corrosion fluctuated greatly, and the same dark corrosion product (pyrosol) was formed around the titanium samples in the salt baths, even at the lowest temperatures used (at 375°C, sample 17A and 17B, Table II). The attack was strongest when the samples were only half immersed in the melt, so that fumes could attack the upper part of the sample. These parts were severely corroded, especially in the presence of potassium chloride. Lithium chloride appeared to be less corrosive. The table shows further that rate of corrosion increased with temperature. As before, in vacuum the rate of corrosion was much less than in the presence of air.

Attack by sodium fluoride.—The greatest loss of weight of the titanium samples due to corrosion resulted from immersion in a mixture of approximately 50% of sodium chloride and 50% of sodium fluoride; this bath at 850°C caused the metal to disintegrate completely in 3 hr, leaving a dark gray powder similar in appearance to that obtained in the previous cases. Attempts to heat the sample in the fluoride bath under vacuum were unsuccessful because the melt attacked the silica glass so strongly that air penetrated into the evacuated tubes initiating a severe corrosion of the titanium samples.

DISCUSSION AND CONCLUSION

Although the phenomenon of corrosion of titanium in fused salt baths at elevated temperatures and the formation of pyrosols resembles in many points the pyrosols as described by Lorenz and Eitel (4), and investigated further by Heymann (7), Farquharson (8), and Cubicciotti (9), there are certain differences. The pyrosols described by previous workers were usually prepared by mixing metals of low melting points in molten baths of their own salts. For example, lead in molten lead chloride expels gray clouds which then disappear completely at higher temperatures, probably by forming a true solution with the molten salt. Upon cooling, the gray metallic fog appears again because of aggregation of the lead particles into larger units. With slow cooling the particle size grows larger. In the case of titanium, however, metallic dispersions are formed in fused alkali salts (salts of titanium itself were not tried), at temperatures far below the melting point of the metal itself. Furthermore, for formation of metallic titanium dispersions, presence of air (oxygen) is necessary, as pyrosol formation in vacuum or under inert gases occurred to a very limited extent. Because of experimental difficulties, no attempt was made to raise the temperatures of the melts above 1000°C, in order to check whether the metallic fog would dissolve completely in the melts, and then crystallize out upon cooling. Nevertheless, the cooled melts with the titanium dispersion resembled salts colored by colloidally dispersed substances (10). The transparent salt near the titanium appeared black to blue, but a part of the metallic dispersion was in the form of coarse powder which settled to the bottom of the crucible (Fig. 2). Regardless of the grain size of these metallic dispersions, the system, molten salt-dispersed titanium, can be called a "pyrosol," and the observed corrosion phenomena are, to a great extent, due to pyrosol formation. The reasons for this kind of corrosion are at present unknown; this action does not seem to be electrochemical in nature, but is related to the oxidation of the titanium in the melt or in salt fumes. It appears that this corrosion is not the same as that observed by Copson (11), who found that electrodes immersed in chloride baths were "pencilled" only during the anodic part of the alternating current cycle.

Results of this study show that corrosion of titanium occurs in molten chloride salt baths in the presence of air even at temperatures as low as 375°C, and that the rate of corrosion increases rapidly with temperature. It is evident that, if titanium could be electrodeposited from such baths exposed to air, there would be a great tendency for the deposit to corrode and disperse in the bath.

ACKNOWLEDGMENT

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

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Potentiometric Titrations in Liquid Ammonia

VII. Characteristics of a "Difference Indicator" Electrode System[1]

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ABSTRACT

Titration of ammonium bromide with potassium and with potassium amide in liquid ammonia has been followed potentiometrically using a "difference indicator" electrode system. It has been shown that neither the precision with which the end-point is detected nor the magnitude of the corresponding change in potential is appreciably influenced by variation in either the length or diameter of the reference electrode capillary. Data relative to the effect of the concentration of supporting electrolyte and the composition of the solution in the reference electrode compartment are presented and discussed.

INTRODUCTION

The use of potentiometric titrations to follow the course of reactions in liquid ammonia was first described by Zintl and coworkers (1). They employed an electrode system of the type described by Muller (2) and which is designated by Kortüm and Bockris (3) as a "difference indicator" electrode system. In this titration procedure, one electrode (the indicator electrode) is immersed in the solution to which the titrant is added; the other (reference) electrode is immersed in solution having a composition the same as the initial composition of the solution to be titrated, but isolated from the latter in a separate compartment that is connected to the main body of the solution by a fine capillary tube.[2]

Following rather extensive modification of Zintl's equipment and procedures (4), this method has been used in these laboratories in the study of a considerable variety of reactions in liquid ammonia in which solutions of alkali metals or alkali metal amides have been used as titrants (5–9). In these studies it has been possible generally to correlate observed changes in potential with either anticipated or reasonable stoichiometry. In a few cases, however, quite anomalous changes in potential have been observed, and it has been suggested that these may be attributable to factors such as changes in composition of the solution in the reference electrode compartment owing to diffusion, concentration of supporting electrolyte, etc. Accordingly, it seemed worth while to investigate the role of such variables and to attempt to establish optimum conditions for the use of this type of electrode system in the study of reaction mechanisms.

For such purposes it is obvious that the reactions involved in the titrations should be simple, rapid, and quantitative, and that all reactants and products should be ammonia-soluble. These requirements are met by the reactions represented by the equations

$$NH_4Br + KNH_2 \rightarrow KBr + 2NH_3$$
$$NH_4Br + K \rightarrow KBr + \frac{1}{2}H_2 + NH_3$$

which are also representative of simple metathesis and oxidation-reduction reactions, respectively. Attention is also called to the fact that these reactions involve species common to all liquid ammonia solutions, i.e., the ammonium and amide ions.

Equipment

The titrator and its auxiliary equipment consisted of a modification of that described previously (4); major modifications were as follows. The vessel for make-up and storage of standard solutions was replaced by a second buret also connected to the titration vessel as described previously; this modification, of course, necessitates making up the standard solutions directly in the two burets. The other change involved provision for the simultaneous introduction of two or more reference electrodes.

The reference electrode is illustrated by Fig. 1(I). The metallic element is a platinum wire (length, 2 cm; diameter, 0.016 in.) sealed through the top of the electrode compartment and contacting a copper lead-wire via a mercury pool (not shown). The electrode-compartment capillary is of uniform diameter for 1 cm from the tip. The capillary diameter was determined microscopically and, in one case, was checked in terms of the weight of mercury contained in a 35 cm length of capillary tubing having a uniform diameter of 0.8 mm. The uniformity and accuracy of the measurement is estimated to be within 3 % of the diameter.

Indicator electrodes are made by sealing platinum

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[1] Manuscript received May 7, 1954.

[2] This type of reference electrode has been referred to previously (4) as a differential electrode. There appears to be no sound objection to this term except that, through inadvertence, it is erroneously interpreted as implying a differential titration procedure.

wire (length, 1 cm; diameter, 0.016 in.) in the end of a Pyrex tube; a general purpose indicator electrode was made similarly from platinum rod (length, 1 cm; diameter, 0.05 in.).

Potentials were measured by the null method using a conventional circuit: L&N Type K potentiometer, Certified Weston Standard cell, Rubicon spotlight galvanometer (current sensitivity, 0.011 μa/mm), and an L&N constant-potential lead storage cell.

An alternate reference electrode, the Hg-Hg^{2+} half-cell, is constructed as shown in Fig. 1(II); since it is involved in only minor respects in the work reported below, this electrode will be described in more detail in a later communication.

Materials

Analytical Reagent Grade ammonium bromide and potassium bromide were recrystallized from triple-distilled water, powdered in an agate mortar, and dried at 110°C. Potassium was double-distilled and stored under dry oxygen-free nitrogen in fragile Pyrex glass ampoules by means of techniques to be described elsewhere (10). Potassium amide was prepared *in situ* by the interaction of potassium and liquid ammonia catalyzed by iron wire. Commercial nitrogen (Linde HP Dry) was completely dehydrated and deoxygenated by scrubbing it through a solution of potassium in liquid ammonia at -33.5°C. Commercial anhydrous ammonia was used directly for thermostating purposes, but that used as a solvent and reaction medium was predried over sodium amide and finally passed through a concentrated potassium solution before use in the preparation of standard solutions. The conductivity of this "solvent ammonia" was $<10^{-6}$ ohm^{-1} cm^{-1}.

PROCEDURE

Scrubber and titration units were cleaned with aqua regia, rinsed with several portions of distilled water, rinsed with ethanol, and dried. Potassium was placed in the scrubber, and the units were assembled (4). The entire system was pumped at 0.03 mm pressure for several hours, filled with "solvent ammonia" gas, re-evacuated, and refilled with ammonia gas just before starting a typical run, which was carried out as follows.

With gaseous ammonia flowing through the system, a bulb containing a known weight of potassium is put into one buret, a weight of ammonium bromide equivalent to the potassium is put into the other buret, and 1.00 g of potassium bromide is placed in the titration vessel. The scrubber is cooled with ammonia, and from 75 to 100 ml of solvent ammonia is condensed therein; this provides a 6–8 in. head of potassium solution, and all gases entering the titrator pass through this unit. The potassium ampoule in the one buret is crushed, the titrator assembly is cooled with ammonia, and about 30 ml of ammonia is condensed in each buret and in the titration vessel. The reference electrode compartment fills during this operation, and the potential is usually constant after 20 min.

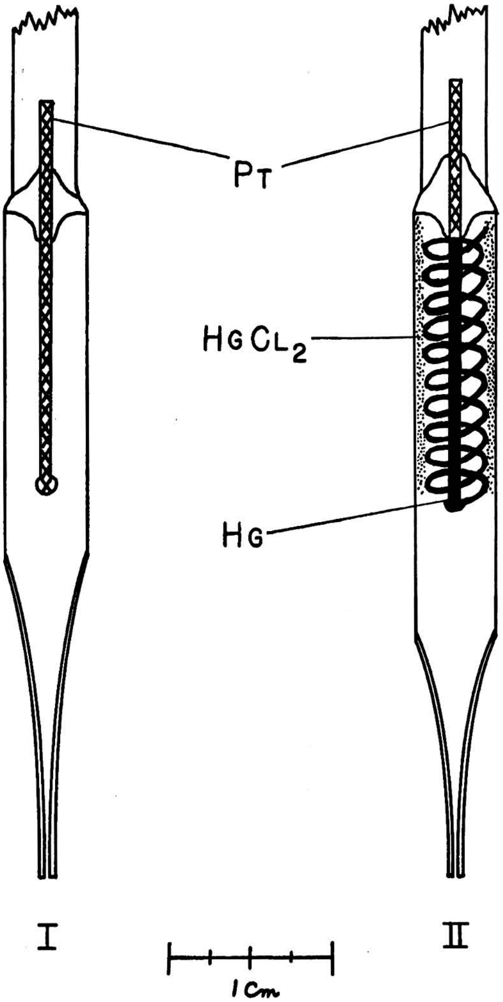

FIG. 1. Reference electrodes. I, The difference indicator electrode; II, the Hg-Hg^{2+} half-cell.

Titrations are carried out by adding solution to the titration vessel from one buret, then titrating this with the solution from the other. Enough time is allowed between the additions of titrant for the potential to become constant. A measured excess of titrant may be added beyond the end-point and the resulting solution back-titrated with the solution in the other buret; this process may be repeated until the supply of one of the solutions is exhausted.

Volume readings are accurate to within 0.05 ml. The accuracy of end-point determinations is about 2%; internal agreement is within 1%. Temperature variations, as indicated by a toluene thermometer, are <1° during the course of a titration; temperatures ranged from −35° to −39° for all of this work. Changes in potential due to temperature changes were less than the precision of potential measurements, which was 5 mv.

RESULTS

Titrations involving reference electrodes having different capillary diameters are represented graphically by Fig. 2, 3, and 4; these correspond, respectively, to the titrations:

$$K + NH_4^+ \rightarrow K^+ + \tfrac{1}{2}H_2 + NH_3 \qquad (I)$$

$$NH_2^- + NH_4^+ \rightarrow 2NH_3 \qquad (II)$$

$$NH_4^+ + NH_2^- \rightarrow 2NH_3 \qquad (III)$$

where the titrant appears first in the equation. Mole ratios shown on the abscissas are calculated from known concentrations of the solutions employed; the points represent the corresponding experimentally measured potentials. The concentration of the titrant varied from 40 to 85 millimolar; that of

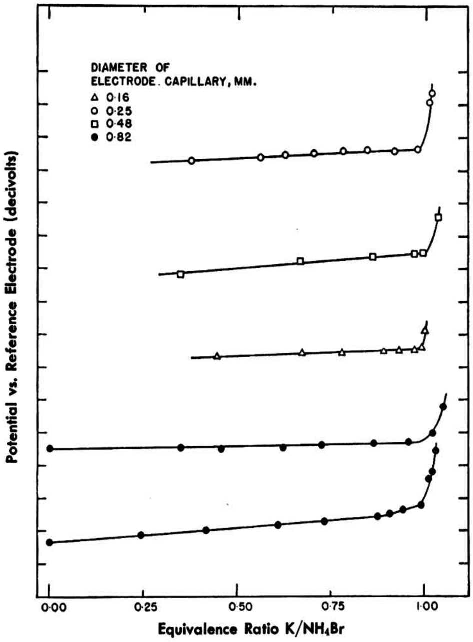

FIG. 2. Potentiometric titrations of NH_4Br with K using difference indicator electrodes having different capillary diameters.

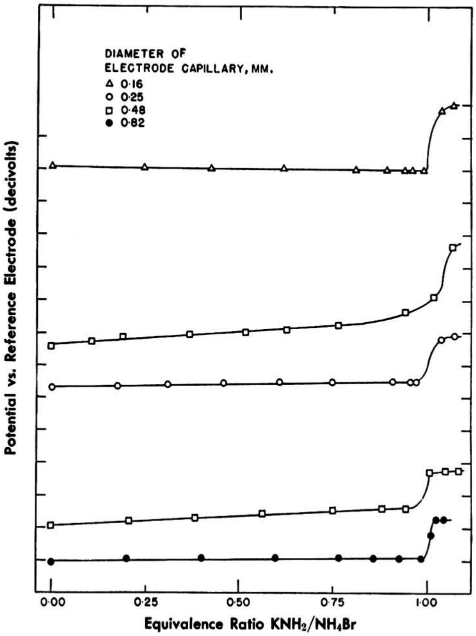

FIG. 3. Potentiometric titrations of NH_4Br with KNH_2 using difference indicator electrodes having different capillary diameters.

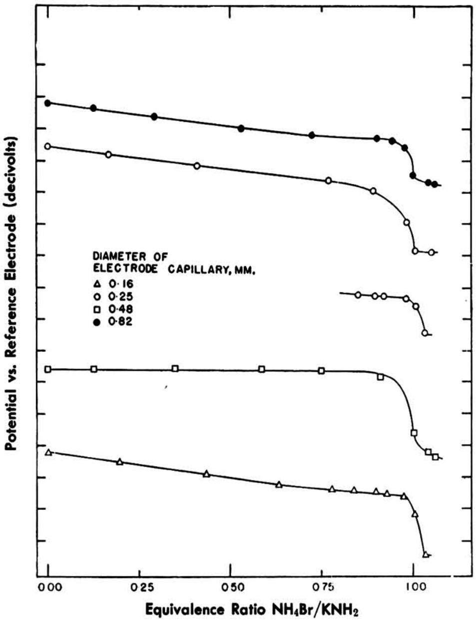

FIG. 4. Potentiometric titrations of KNH_2 with NH_4Br using difference indicator electrodes having different capillary diameters.

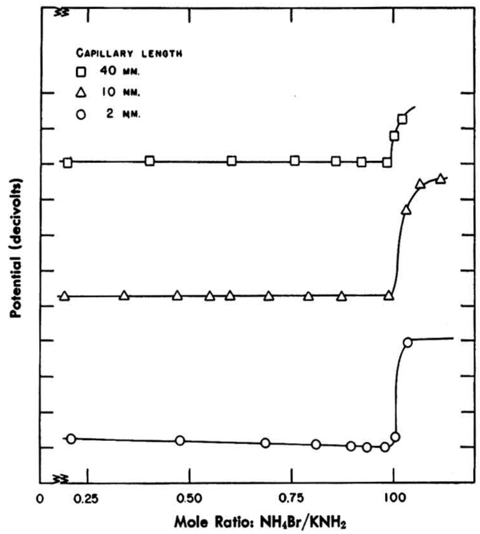

FIG. 5. Potentiometric titrations of KNH_2 with NH_4Br using difference indicator electrodes having different capillary lengths.

the solution being titrated varied from 5 to 20 millimolar. The time required for a single titration was about 2 hr. The potential scale in Fig. 2, 3, and 4 is divided into 0.1 v units, and no attempt is made to relate "absolute potentials" for different titrations. Initial potentials were not reproducible, except for random cases, even when extreme precautions were taken to insure conditions as nearly identical as possible. In some cases, initial potentials varied by as much as 0.6 v; even two indicator electrodes in the same solution would, at times, show a potential difference of 0.4 v. However, the magnitude of the total potential change at the end-point was about the same for the same titration with different reference electrodes.

When the reference electrode contained potassium solution, anomalous results were obtained. These varied from the extremes of a stable reference potential to a rapidly dropping potential accompanied (within 5 min) by a discharge of the blue color characteristic of the potassium solution.

Neutral solutions of supporting electrolyte in the reference electrode sometimes resulted in a titration curve with an anomalous break preceding the correctly indicated end-point. This occurred most frequently in titration (III), for which this break also frequently appeared when acidic or basic solutions were present in the electrode compartment. Otherwise, acidic and basic solutions in the reference electrode gave quite reproducible results, except for the values of the initial potentials.

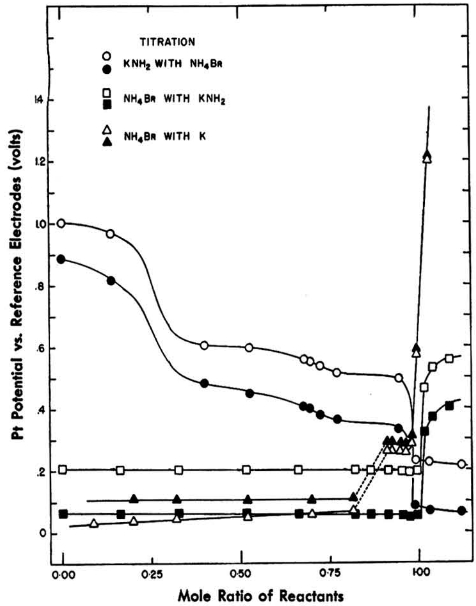

FIG. 6. Potentiometric titrations followed simultaneously with the difference indicator electrode (solid points) and the Hg-Hg^{2+} half-cell (open points).

A reference electrode with a capillary diameter of 0.8 mm was used to investigate the effect of capillary length on the reproducibility of end-point determinations. Results of titrations employing this type of electrode with a capillary of uniform diameter and 2, 10, and 40 mm in length are shown in Fig. 5.

In order to determine the effect of supporting electrolyte concentration on the sensitivity of the potential measurements, titration (III) was followed by means of a reference electrode (capillary diameter, 0.16 mm) in a run without supporting electrolyte. To 25 ml of ammonia was added 8.0 ml of 0.0642N potassium amide solution; the electrode was filled, and the solution was titrated with 0.0660N ammonium bromide solution. The emf sensitivity was ±15 mv and the end-point indicated was 8%[3] beyond the stoichiometric end-point. To this dilute potassium bromide solution was added 9.0 ml of potassium amide solution, the electrode was refilled, and this solution was titrated with the standard ammonium bromide solution. The emf sensitivity in this case was ±8 mv, and the titration error was reduced to 6%. The electrode was again refilled after addition of 9.5 ml of the amide solution, and in the ensuing titration the emf sensitivity

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[3] Estimation of error is made on the basis of the total quantities of the two solutions added; hence, this factor is cumulative.

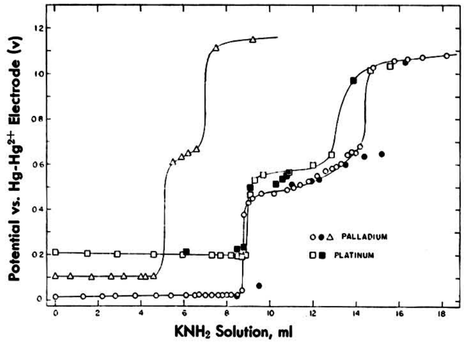

FIG. 7. Indicator electrode behavior in acidic and basic media.

was ±5 mv, and the end-point was determined to within 1%.

Titrations (I), (II), and (III) were followed simultaneously with a reference electrode having a capillary diameter of 0.25 mm and with the Hg-Hg^{2+} half-cell; results are shown in Fig. 6. The emf sensitivities were ±10 mv and ±0.1 mv, respectively. The potential difference of the two reference electrodes could be determined with a precision of ±10 mv, and it changed at a rate of about 5 mv/hr over a period of several hours.

Since the electrode reactions that occur at the indicator electrode may be expected also to function at the metallic element in the reference electrode compartment, the behavior of the indicator electrode was checked against the Hg-Hg^{2+} half-cell reference potential. Titration (II) was carried out with potassium amide solution additions carried far beyond the stoichiometric end-point, and the resulting solution was back-titrated as in titration (III). Results are shown in Fig. 7, where the open points are for (II) and the solid points correspond to (III); here, again, changes in potential from the lower to the middle plateau are in good agreement with the calculated stoichiometric end-points. Although not shown in Fig. 7, the change from the middle to the upper plateau appears to be sensitive to amide ion concentration, and the potential behavior during the transition is suggestive of a very easily polarizable electrode. Results are quite reproducible if the indicator electrode is exposed *in situ* to a dilute potassium solution prior to the titration; otherwise, the upper plateau may not appear.

DISCUSSION

In designing the experiments reported above, the precision sought has been limited by the lack of data on electrode reactions in liquid ammonia. The half-cells that have been described in the literature were rejected on the grounds that they involve experimental complexities of an order not compatible with the relatively simple equipment and procedures employed in this work. It is considered sufficient that the present titrations show indicated end-points in quite good agreement with the stoichiometric end-points.

Data of Fig. 2, 3, and 4 show that variation of capillary diameter has no detectable effect upon the accuracy of determination of the end-point using capillaries in this range of length and diameter. With the possible exception of the amide solution, the cell potential is essentially constant with small changes in concentration; only at the end-point, where there is a very large change in the relative ratio of reactants, is there an appreciable abrupt change in potential. The drift in potential in titration (III), Fig. 4, is seen in Fig. 7 (middle plateau[4]) to be attributable to changes in the potential of the indicator electrode. Thus, it may be concluded that the potential of the reference electrode is constant during these titrations.

The variation of capillary length, with the capillary of largest diameter used in any of this work, has no effect on the accuracy of the end-point determination, or the reliability of the reference electrode under the conditions of the titrations illustrated by Fig. 5. It may also be expected that a variation in length between 2 and 20 mm would not have adverse effect on capillaries with a diameter between 0.2 and 0.8 mm.

The composition of the solution in the reference electrode compartment was found to be of importance in only two cases. Despite a reproducible initial cell potential near zero, potassium solutions in this compartment in many instances undergo catalytic decomposition at the platinum electrode element. Although the relative rate of this reaction is low, the volume of this solution is <0.5 ml, and it undergoes a rather large change in concentration; thus the reference potential changes considerably. Titrations followed with an electrode containing a neutral solution, and in some instances showing a premature change in potential along with a correctly indicated end-point, may be explained on the assumption that the composition of the electrode solution is the same as that of the solution at the transition point between the middle and upper plateaus, as shown in Fig. 7. The actual change is caused presumably by the polarization of the reference electrode; in the cases mentioned, the magnitude of change in potential is in agreement with this explanation. In view of these findings, it is suggested

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[4] As may be seen from Fig. 6 and 7, the potential of this plateau identifies it with the NH_4^+-H_2 electrode reaction. The potential of the upper plateau is probably that of the NH_2^--N_2 half-cell with an appreciable overvoltage (11).

that acidic or basic solutions provide the most suitable reference electrode components.

Results obtained upon variation of the concentration of supporting electrolyte are in keeping with those expected because of low electrical conductivity (12). Comparison of results obtained simultaneously with two different reference electrodes vs. a common indicator electrode (Fig. 6) show that the sluggishness of response in measurements involving the difference indicator electrode may be attributed almost exclusively to that electrode reaction rather than to either the capillary characteristics or the indicator electrode.

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FUTURE MEETINGS OF

The Electrochemical Society

Cincinnati, May 1, 2, 3, 4, and 5, 1955

Sessions probably will be scheduled on

Electric Insulation, Electronics, Electrothermics and Metallurgy, Industrial Electrolytics, Theoretical Electrochemistry

Headquarters at the Sheraton-Gibson Hotel

★ ★ ★

Pittsburgh, October 9, 10, 11, 12, and 13, 1955

Headquarters at the Statler Hotel

★ ★ ★

San Francisco, April 29 and 30, and May 1, 2, and 3, 1956

Headquarters at the Mark-Hopkins Hotel

★ ★ ★

Cleveland, October 28, 29, 30, and 31, and November 1, 1956

Headquarters at the Statler Hotel

★ ★ ★

Washington, D. C., May 12, 13, 14, 15, and 16, 1957

Headquarters at the Statler Hotel

★ ★ ★

Buffalo, October 6, 7, 8, 9, and 10, 1957

Papers are now being accepted for the meeting to be held in Cincinnati. Triplicate copies of each abstract (not exceeding 75 words in length) are due at the Secretary's Office, 216 West 102nd Street, New York 25, N. Y., *not later than January 15, 1955.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

Current Affairs

Boston Meeting in Review

The 106th meeting of The Electrochemical Society held in Boston on October 3 to 7, 1954, was the best attended fall meeting in the history of the Society. A total of 667 persons registered.* This was just slightly less than the all time high at the last Chicago meeting but 67 more people than the *maximum* number the local committee had been assured could possibly attend. All is forgiven, however, since all ended well, thanks largely to the extra capacity and fine organization of the Statler Hotel. The Society had the whole mezzanine floor which made it seem very private and assured the meeting of our old friends. The chatting on quiet divans around the mezzanine gave all the evidence needed that the meeting was accomplishing one of its main objectives.

There was a surprisingly large number of members of long standing "back" for the meeting; to mention just a few—Mrs. Colin Fink, Mr. and Mrs. F. C. Mathers, A. T. Hinckley, Mr. and Mrs. George W. Vinal, H. J. Creighton, and M. O. Sem.

There was also a large group from outside the U. S. A.—about 20 in all—from England, Belgium, The Netherlands, and Norway, among others. Some of these had been invited to present papers at the symposia and their presence added a very distinctive touch to the meeting.

The large registration was undoubtedly due to the particularly fine programs for which the chairmen of the divisions and their speakers deserve great credit. The program was so good in fact that it brought out a large group of nonmembers, many of whom were local registrants who to our knowledge had never previously shown interest in the Society. Many applications for membership were filled out at the Registration Desk and, if all those who took a blank return it, the membership increase should be substantial. (One man took five, muttering about the people in his lab who had better join!)

To insure that all could hear the program, even when the speaker or a questioner from the audience moved away from the podium, the local committee bought and gave to the Society for future meetings three portable hand microphones to be used with regular amplifying systems.

Extended abstracts of the Battery Division went like hotcakes. Judging from the number of people who almost bought them thinking they contained abstracts from other divisions, there seems to be great interest in this technique. Sensing a future trend, several members of the Theoretical and Battery Divisions met with some of the Electronics Division to exchange ideas and findings based on their experience with abstracts. They agreed to keep in touch and offer assistance to any of the other divisions considering publication of abstracts in future sessions.

Plant trips proved very popular, probably because they had been based on direct suggestions of division chairmen and because they were scheduled so as not to conflict with the technical sessions. Visits were made to Ionics, Inc., to see an exhibit of electrolytic ion exchange membranes; to Arthur D. Little, Inc., to see their new laboratories and hear a discussion of the application of operations research to corrosion problems; to the Watertown Arsenal for a visit to the electroplating laboratory; to the National Research Corporation for the viewing of the manufacture of high vacuum furnaces and equipment; and to Herb Uhlig's Corrosion Laboratory at M.I.T. All were sell-outs (44 persons) and several times late comers, who had either missed connections for the bus or arrived too late to sign up, departed in search of taxis to take them anyway.

For the ladies who came to the Boston Meeting the days were very full, beginning each morning with a get-together over coffee. On Monday afternoon there was a trip to Concord with its Antiquarian Society and the homes of the Alcotts and Hawthorne. It was a perfect autumn day on Tuesday for the shore trip to Rockport, Salem, and Marblehead. En route were beautiful views of the ocean, as well as glimpses of picturesque narrow streets and handsome examples of early American architecture. In spite of drizzle on Wednesday, thirty ladies visited the restored Iron Works at Saugus before lunching at the Towne Lynne House. They arrived back at the Statler in time for a short rest and then went to the M.I.T. Faculty Club for tea. The sun came out brightly and from across the Charles River they had a splendid view of the gold dome of the State House, surrounded by the red brick which is Boston. The program ended with coffee Thursday and a feeling that all had been happily steeped in New England antiquity. One of the lady guests was overheard to tell her husband she had had so much fun in Boston that even if he had no interest in the Cincinnati Meeting, they were going anyway!

On Monday, the Society heard a most interesting talk by Professor Donald H. Menzel, Director of the Harvard College Observatory. Dr. Menzel stated that . . . "there is nothing in all of the evidence that has been collected about flying saucers to justify in any degree the view that we are suffering from a visitation of flying saucers from outer space. Natural phenomena responsible for flying saucers sightings number in the hundreds and no single theory suffices for explanation." In his talk, which was entitled "What's New About Flying Saucers?," Professor Menzel traced the past, present, and future of the flying saucer scare, which dates to about 800 B.C. Among the natural phenomena that result in flying saucer reports, he explained, are: reflections of ice crystals, mirages, aurora borealis, bright fire balls or meteors, reflections from spider webs or bird feathers, or even owls or bats covered with a luminous fungus that makes rotten wood glow in the dark.

An outstanding feature of the meeting

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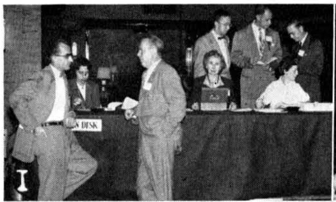
* For those interested in statistics: 289 members, 306 guests, 59 ladies, 13 students.

was the Acheson Memorial Dinner. Dr. N. M. Winslow introduced Mr. George W. Heise with a very human accounting of Mr. Heise's outstanding career as both man and scientist. Mr. Heise then delivered his Acheson Memorial Lecture with a stimulating discussion of fuel cells and scientists who resist the temptation to become administrators, concluding with a quotation from Noel Coward to express his feelings "on the advantages of being extinct." At the Society dinner on Wednesday A. C. Makrides, second prize winner of the Prize Essay Contest, was present to receive the applause of those attending.

At the Wednesday night Society Dinner, Mr. Harold E. Edgerton, Professor of Electrical Measurements at M.I.T., presented a first-hand account of his descent in the Bathyscaphe, a deep-diving submarine built by the French Navy. He showed motion-picture films taken during the summers of 1953 and 1954 in the Mediterranean, while a member of the crew of the research ship, the "Calypso," under the command of Commandant Jacques Y. Cousteau, author of "The Silent World."

The main object of Edgerton's effort was to study methods of getting information on the so-called Deep-Scattering-Layer and on the bottom of of the sea. Several methods that have been devised and used were shown on slides and movies. During the course of the investigation, specially designed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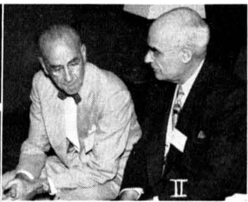
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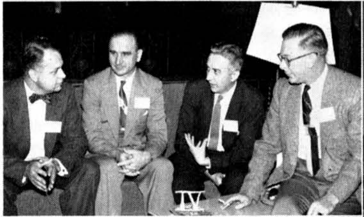
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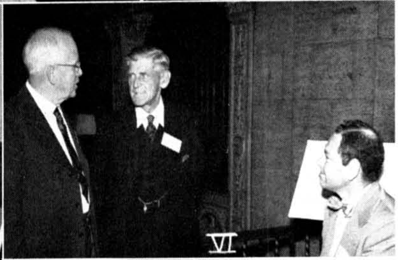
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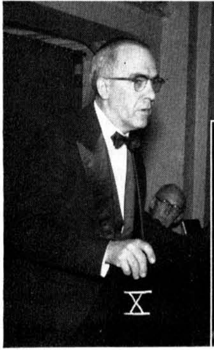
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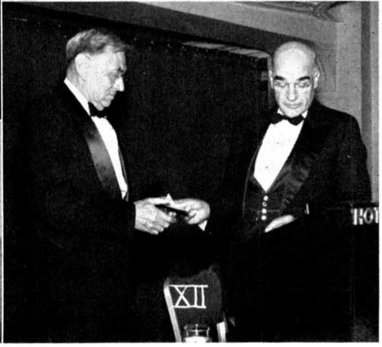
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I—Seated behind the Registration Desk are Anne C. Smith, secretary to S. E. Eaton; standing behind the desk, R. C. Wade, S. E. Eaton, and H. H. Homer; in front of the desk are A. E. Middleton and I. E. Campbell. II—R. M. Hunter and M. J. Udy. III—Society Headquarters Office, behind the table, H. B. Linford, R. M. Burns, J. K. Maddock; in front of the table, A. E. Middleton, R. G. Sterns, M. J. Udy, and N. Michalski. IV—E. J. Smith, J. M. Manko, J. K. Sargent, and R. A. Woofter. V— Standing, Howard Acheson, Mrs. Margaret Stevens (Mr. Heise's daughter), and George W. Heise; seated, Mrs. Acheson, Mrs. L. Stuart (Edward Goodrich Acheson's daughter), and Mrs. Heise. VI—F. C. Mathers, H. J. Creighton, and Morton Schwartz. VII—M. O. Sem, R. M. Burns, and Mrs. Lottie Fink. VIII—T. D. McKinley, C. W. Jerome, and H. H. Homer. IX—H. J. Strauss, A. T. Hinckley, and N. M. Winslow. X—N. M. Winslow giving the talk about the Acheson Medalist, G. W. Heise. XI—Milton Janes, Sherlock Swann, A. K. Graham, and C. L. Faust. XII—M. J. Udy presenting the Edward Goodrich Acheson Medal to G. W. Heise.

electronic flash equipment capable of operating at depths of two miles was installed on the Bathyscaphe. Cousteau's group of divers are currently excavating the wreck of a Greek cargo vessel that was sunk about 100 years B.C. near Marseille, France. Professor Edgerton, assisted by his wife, projected slides showing the progress of this effort.

Those attending the Wednesday Dinner were also privileged to hear a group of local close-harmony enthusiasts. The audience literally held its breath while they diminished one "fifth" after another. Most of the group were professional men—some even electrochemists. Their harmony was so close you actually felt you were a part of it. One member of the audience got so excited he dashed out after the last encore to try to drag the group back for more!

An experiment in cocktail arrangements was voted a success for both dinners. The Statler's top quality cocktails were sold for 25¢ apiece, thus pleasing both nondrinkers (definitely in the minority) who didn't feel they were paying for the drinks of others and the imbibers who felt they were getting a bargain.

All in all the meeting seemed to be a great success. It aroused so much interest, in fact . . . that there is a determined effort under way in Boston to organize a local chapter of the Society and this time we hope it will succeed.

DIVISION NEWS

Luminescence Symposium, May 1955

The annual Luminescence Symposium of the Electronics Division of The Electrochemical Society will be held during the week of May 2, 1955, at the 107th meeting of the Society in Cincinnati, Ohio.

Detailed plans for the Symposium have not been set and, in fact, cannot be until titles and abstracts of papers have been received by H. Bandes, Vice-Chairman (Luminescence Group), Electronics Division, Sylvania Electric Products Inc., Bayside, N. Y.

A 75-word abstract, to be printed in the general program for the meeting, will be required by *January 15, 1955*. In addition, an "expanded abstract" of about 1000 words, along with curves, data, etc., will be due not later than *February 1, 1955*. This latter abstract will be "printed, not published" in the booklet of "Enlarged Abstracts of Papers Presented by the Electronics Division" which will be available both from the Secretary of the Division, and at the meeting, at cost.

The work of your Symposium Chairman will be greatly facilitated by early notification of your intention to present a paper and by early receipt both of short and expanded abstracts.

Present plans indicate that there will be at least a two-day Symposium with one half day reserved for a Round-Table discussion and the remaining day and a half to be spent in separate, but not concurrent, sessions devoted to: (*a*) basic principles and phenomena, and (*b*) specific phosphor chemistry, structure and behavior.

Dr. Ferd E. Williams, Research Laboratories, General Electric Company, will deliver the keynote talk and will act as Chairman of the basic principles session(s).

Following past practice, 20 to 30 minutes (including discussion) will be allotted each paper.

Following the plans of the Semiconductor Symposium of the Spring 1955 meeting, an attempt will be made to provide for 10-minute "late news" presentations. A deadline date of April 8, 1955, will allow for publicizing these "late news" items at least by mail to the members of the Division.

The Phosphor Screen Application Group, which was incorporated into the Luminescence Group in May, is organizing its own Symposium under the chairmanship of Dr. C. Dichter, General Electric Company, Syracuse, N. Y. The scope of the Group has been enhanced by deletion of "Screen" from its name.

H. Bandes, *Vice-Chairman*
(Luminescence Group)

Semiconductor Symposium Planned for Cincinnati

The Semiconductor Group of the Electronics Division is making plans, to hold the third annual Semiconductor Symposium during the Cincinnati Meeting, May 1 to 5, 1955.

At present, plans are to divide the sessions as follows: two half-day sessions on semiconducting materials—elemental, alloys, and compounds; one half-day session on surface controlled phenomena; and one half-day session on chemical process technology.

Anyone wishing to present a paper at this symposium should have contacted F. J. Biondi, Bell Telephone Laboratories, Murray Hill, N. J., by December 1, signifying interest in participating and title of proposed papers.

No later than January 14, 1955, submit a 75-word abstract for inclusion in the program booklet. *No later than February 1, 1955,* submit a second "extended abstract" of about 1000 words, including brief pertinent data, curves, and illustrations. This extended abstract is "printed, but not published" in a booklet "Enlarged Abstracts of Papers Presented by the Electronics Division" and will be sold at the Cincinnati Meeting.

Symposium Planned by Metallurgy Section of the E & M Division

The Electrothermics and Metallurgy Division is scheduling a Symposium on "Electrochemical Techniques in Metallurgical Research" for the Spring Meeting of The Electrochemical Society to be held in Cincinnati, Ohio, May 1–5, 1955.

The scope of the Symposium will include: Metallography, Thermodynamics, Electroanalysis, Preparation of High Purity Metals, Atom Movements, and Electromachining.

Contributions for this Symposium are invited from all interested persons. It is desired that papers be contributions of original research and not merely reviews of a portion of the subject field.

Abstracts (not to exceed 75 words in length) and correspondence should be submitted *not later than January 3, 1955,* to the Chairman of this Symposium, Dr. J. H. Westbrook, General Electric Research Laboratory, The Knolls, Schenectady, N. Y.

Symposium on Fused Electrolytes

The Theoretical Electrochemistry and Industrial Electrolytic Divisions of The Electrochemical Society are planning a symposium on "Fused Electrolytes" for the spring meeting of the Society in Cincinnati on May 1–5, 1955. The first day of the symposium will include invited papers on fundamental aspects, as well as a round-table discussion. A number of contributed papers will also be presented at the symposium.

Those people interested in submitting contributed papers should send two copies of a 75-word abstract to the Secretary's office, 216 West 102nd Street, New York 25, N. Y., and two additional copies to Ernest Yeager, Department of Chemistry, Western Reserve University, Cleveland 6, Ohio, *not later than January 15, 1955*. Extended 1000-word abstracts are also planned for the symposium. Contributors to the symposium will be notified concerning the extended abstracts after January 15 1955.

SECTION NEWS

Chicago Section

The first meeting of the season was held on October 1, 1954, at the Chicago Engineer's Club, with Ben F. Freeberg, Local Section Chairman, presiding. There were two speakers for the evening: Howard T. Francis of Armour Research Foundation discussed "Plating from the Point of View of Corrosion" and Bernard C. Case of the Sunbeam Manufacturing Company spoke on "Corrosion from the Point of View of the Plater."

Dr. Francis pointed out the basic requirements of protective metallic coatings, and showed several advantages of electroplating as a means of applying coatings. An ideal coating is one which completely isolates the material from the environment and does not itself corrode. The biggest problem in providing such protective coatings is characteristically that the metallic coating is porous and the corrosive environment can penetrate t and contact the substrate material. He pointed out that for this reason the most successful electroplating protection is achieved only when the plate sacrificially protects the underlying metal. It is also necessary, of course, that even while acting as sacrificial anode, the plate itself must not corrode too rapidly.

Several anomalies were then described in which the behavior of plated materials was not that which might have been expected. Some instances were given in which the current in couples was observed to flow in the opposite direction from that predicted by the open circuit potentials. The reversal of the polarity of the tin-steel couple upon adding oxygen to a deaerated solution was described.

Mr. Case devoted his discussion largely to copper-nickel-chromium plates. The big problem in such plates is localized attack, or pitting, through it. This effect is quite irreproducible, there frequently being more variations among samples in a batch than between batches. Improvement has consequently been difficult and the plating industry has been forced to operate on a statistical basis. Mr. Case outlined current trends in thinking with the objective of improving uniformity of such plates.

Apparently many plates are not porous as produced but become so under the influence of the corrosive environment. Under these circumstances the problem appears to be one of producing an essentially homogeneous surface of the metal. For the purpose of getting nickel plate which is nonporous and has a uniform potential, electropolishing the base metal is a good pretreatment, the copper flash is of doubtful value, an iron flash is definitely beneficial, high temperature baths are beneficial, and reverse current practices are beneficial.

J. E. Draley, *Secretary*

On November 5, 1954, Samuel W. Bradstreet, Jr., of Armour Research Foundation addressed the members of the Chicago Section of The Electrochemical Society on "Solution Ceramics."

In this novel application, decomposable salts of certain metals are sprayed onto a hot metal surface. The solution evaporates, forming very tiny particles of the salt which decompose to oxides. The oxide coatings formed in this fashion are adherent, smooth, and thin, having colors depending upon their composition. They show no patterns in x-ray or electron diffraction, apparently being composed of very tiny crystallites. Properties of the coatings are independent of the temperature. They are not flexible bodies, but apparently can stretch on metal so that when the base metal is flexed the ceramic coating is not damaged. They can withstand thermal shocks quite well: if molten iron is poured on a ceramic coating it is not damaged. They possess unusual combinations of conducting properties. For example, the solution ceramic coating of CrO_3 is an excellent thermal insulator but has an electrical resistivity of about 1 ohm-cm. Zirconia makes a poor thermal insulator but an excellent electrical insulator.

It appears that there will be widespread applications for these ceramic coatings. A few uses are as lining for molds, as priming coats for nonadherent lacquers and waxes, as base coat substitutes for enamels and glazes, as reflective and insulating coatings to protect metals against radiant heat or contact with molten metals, reactive solids or viscous fluxes or glasses.

J. E. Draley, *Secretary*

Ontario-Quebec Section

The first meeting of the Ontario-Quebec Section was held at McGill University in Montreal on Friday, October 1, 1954, at two o'clock in the afternoon. The speakers were Mr. Charles Vokac, Manager, Hydro Arc Furnace Department of the Whiting Corporation, who spoke on "Modern Electric-Arc Furnace Controls and Their Development," and Mr. H. S. Newhall, Manager of the Electrothermic Division of the Pittsburgh Lectromelt Furnace Corporation, whose paper was entitled "Electric Furnaces in the Ferro-Alloy Industry."

It was pleasing to have an unexpectedly large turnout of 70 people for the initial meeting. Dr. John Convey, Chairman of the Section, opened the meeting with a brief history of the organization of the Section and its aims and hopes. Dr. G. G. Hatch introduced the speakers. A very good discussion ensued after each paper and the questions were most capably handled by the authors. Many expressions of approval of the meeting and appreciation of the formation of a section were received from those present.

John Sumner, *Secretary*

San Francisco Section

The November meeting of the San Francisco Section was held on November 17, 1954, at the Faculty Club, University of California, Berkeley. The dinner and meeting were attended by 35 members and guests.

The speaker was Mr. D. V. Doub, Industrial Power Engineer of the Pacific Gas and Electric Company, and his topic was "New Developments in Electronics." The talk covered, from a nontechnical point of view, a number of applications of electronics in industry and in the home, such as radio frequency heating, use of radio communication as a production tool, supervision by wired television, applications of ultrasonics, computers, food sterilization, transistors, etc. A lively question period followed the presentation.

In addition to the speaker, the Section had as a guest of honor Dr. R. B. Mears, Director of the Applied Research Laboratory of U. S. Steel Corporation, who was visiting this area.

Morris Feinleib, *Vice-Chairman*

Washington-Baltimore Section

The Washington-Baltimore Section met on October 21, 1954, at the National Bureau of Standards, and had as guest speakers Dr. G. L. Pearson of Bell Telephone Laboratories, whose topic was "The Bell Solar Battery," and Dr. A. M. Moos of Patterson, Moos and Company, who spoke on "Radioactive Batteries."

Dr. Pearson, co-inventor of the Bell Solar Battery, described it as a *p-n* junction photovoltaic device with an over-all efficiency of 6% for converting solar radiation directly into electrical energy. The maximum output from such a battery is 60 watts/m^2 for a clear day with a yearly average of 10 watts/m^2. Actually the batteries constructed have had maximum outputs of 1 watt or less.

The origin of charge in the solar battery is a *p-n* junction formed on a silicon surface by alloying. Dr. Pearson described the construction of such photosensitive devices, and the mechanism of charge utilization in the solar cell. In full sunlight the open circuit potential is about 0.5 v and the short circuit current is 25 ma/cm^2. Typical electrical characteristics of the Bell Solar Cell were described. The maximum power output from a cell of 1 cm^2 area is 6 milliwatts at an output voltage of 0.3 v and a load resistance of 15 ohms. The natural limitations on the efficiency of such devices include the loss through reflection, the losses through internal adsorption, and the photovoltaic characteristics of the material itself.

Solar batteries have been used to power portable FM transmitters and repeaters of rural carrier telephone systems. Another proposed use is in photographic exposure meters. The lecture concluded with a demonstration of solar battery powered telephone hand sets.

Dr. Moos gave a most lucid survey of the field of radioactive batteries; what outputs can be expected from them and what limitations are inherent in the present designs. Ideally, a radioactive battery could have a long useful life depending upon the half-life of the active material. Such a battery would be unaffected by temperature, pressure, humidity, or even chemical changes. And, finally, such a battery could be made small, simple, and rugged. Radioactive batteries are by nature of low efficiency and useful only for minimum current drain. Dr. Moos discussed several radio isotopes of possible use in batteries. Among the considerations are shielding against secondary radiation; the half-life of the isotope chosen; and the effects of emitted particles, rays, and other isotopes, and their decomposition products. Mentioned as possible sources were strontium 90, thorium 229, tritium, and carbon 14.

The conversion of the radioactivity of fission by-products into useful electrical power is possible by three methods at the present time—electrostatic, gas ionization, and *p-n* junction devices. The first, electrostatic, reported by Moseley in 1913, consists of two electrodes, one a radioactive electron emitter, and a vacuum or solid dielectric. Recent work has been with sheets of polystyrene or mica as dielectric. The insulator characteristics do change with the strength of the emitter, and this appears to be a limiting factor in these constructions.

These batteries may be used as charge sources for ionization chambers, timers, Ordnance applications, and for maintaining a capacitor at constant charge at relatively high voltage.

The electrostatic battery has the following characteristics.

Activity Sr^{90} millicuries	Current amp	Equilibrium voltages
1	4×10^{-12}	>5,000
3	12×10^{-12}	>7,500
10	30×10^{-12}	>10,000
20	55×10^{-12}	>10,000

The gas ionization radioactive battery consists of two electrodes of dissimilar metals with an ionization gap between them. Gas ions are produced in the gap by bombardment with emissions from a radioactive source. The potential caused by the dissimilar work functions of the two electrodes causes current to flow through the cell, provided the circuit is complete.

The maximum efficiency of this battery type using the best assumptions for electrode treatment, nature of the surface, and collection efficiency is 4.7%.

Compared to electrostatic radioactive cells, the ionization cells are low voltage, high current devices; the voltage being 1 v/cell with currents of 10^{-10} amp/millicurie of radioactive material.

The third type of radioactive cell depends upon the electron voltaic effect of *p-n* junctions similar to the photovoltaic effect described earlier in the program by Dr. Pearson. The voltage and current characteristics are also similar to the solar device. The main difference is that hole-electron pairs are produced throughout a much greater volume of material when nuclear radiations are used for excitation. At present these cells are experimental only and show promise if radiation damage to the *p-n* junction can be minimized. An experimental cell of this type showed an efficiency of 0.4%, and calculations indicate that improvements may result in efficiencies of 2%.

The program was concluded with a discussion period after which refreshments were served.

Jeanne Burbank, *Secretary-Treasurer*

NEWS ITEMS

Nuclear Engineering and Science Committee Organized

The creation of the General Committee on Nuclear Engineering and Science was recently announced. The new body, organized under the sponsorship of Engineers Joint Council, has been established to "meet the pressing problems of nuclear engineering and the related sciences," with emphasis on the "industrial usefulness" of atomic power.

The Council is constituted of eight leading engineering societies with a total membership of 170,000. The American Chemical Society, which has joined the engineers in the nuclear unit, has 70,000 members. Dr. John R. Dunning, Dean of Engineering at Columbia University, has been elected Chairman of the General Committee. Dr. Donald L. Katz, of the University of Michigan, is Secretary and Program Chairman.

The General Committee on Nuclear Engineering and Science stated that it had invited the participation, as members, of organizations of physicists and others concerned with nuclear development.

The General Committee plans a Nuclear Congress to be held July 11–16, 1955, with an expected attendance of 1500. The holding of this Congress, however, is conditioned on the action of the United Nations on the proposal of Secretary of State Dulles for an international conference on the creation of a world bank of fissionable material for peaceful productivity.

"It is the earnest desire of the General Committee on Nuclear Engineering and Science to cooperate fully with such a program," said the new Committee's announcement. "If the United Nations designates a city in North America for a conference in 1955, we shall forego our own Nuclear Congress for that year and we shall be willing to accept the responsibilities for the civilian aspects of the meeting. If the UN conference is held abroad, our Nuclear Congress will be held in a city in the United States to be designated later."

"In the membership of 240,000 of the eight major engineering societies in Engineers Joint Council and of the American Chemical Society are several thousand skilled engineers and chemists who are engaged on the critical problems of mining, processing, and use of all the materials involved in the production of energy by fission. If the Nuclear Congress is not held in 1955 in the circumstances indicated above, the committees and divisions of the societies constituting the General Committee will be urged to hold their own sessions on nuclear matters at their regularly scheduled meetings. If the Nuclear Congress is held, technical papers scheduled for the Nuclear Congress will be prepared by the individual societies through their divisions or committees concerned with nuclear power."

"Nuclear energy is well on the way to having a major role in peace time industrial usefulness. The General Committee provides an organized means of developing discussions and the publication of worthwhile papers and addresses in a field which cuts across all branches of engineering and science."

Organization of the Committee on Nuclear Engineering and Science is a further development of a Nuclear Congress sponsored by the American Institute of Chemical Engineers which was held in Ann Arbor in June 1954.

Besides Dean Dunning and Professor Katz, members of the General Committee include Alex D. Bailey, Manson Benedict, Raymond J. Faust, Jewell M. Garrelts, Augustus B. Kinzel, D. C. MacMillan, Philip N. Powers, J. C. Warner, and Julian D. Tebo.

Engineers Joint Council, which is headed by Thorndike Saville, Dean of Engineering, New York University, is composed of the American Society of Civil Engineers, American Institute of Mining and Metallurgical Engineers, The American Society of Mechanical Engineers, American Water Works, American Institute of Electrical Engineers, The Society of Naval Architects and Marine Engineers, American Society for Engineering Education, and American Institute of Chemical Engineers.

"Modern Electroplating"

Now that the second edition of "Modern Electroplating" has been successfully launched, the Electrodeposition Division is already beginning to formulate plans for a third edition. Although it will undoubtedly be quite a few years before the actual preparation of a third edition will be appropriate, it is not too early for interested parties to point out any specific errors or omissions which they have noted in their perusal of the book.

It is suggested that any reader will be performing a service if he will point out such errors or make specific criticisms or suggestions. For this purpose, Dr. F. A. Lowenheim has been designated as the clearinghouse for such correspondence, which should accordingly be addressed to him at P.O. Box 471, Rahway, N. J., or, alternatively, it may be sent directly to the publisher.

No technical book is ever published that is completely free of errors, but it is the aim of the Division to make "Modern Electroplating" as perfect in this respect as is humanly possible.

Government Research Reports Available

Manufacturers and research laboratories are urged to make more use of the growing stockpile of research reports released by the Federal Government through the Office of Technical Services (OTS) of the U. S. Department of Commerce, Washington 25, D. C.

The government is conducting or sponsoring scientific and technical research at a current rate of more than $2 billion a year, mostly for defense purposes. By far the largest share represents applied research and development. This research generates a vast amount of nonconfidential technical information that is available to businessmen who are interested in developing new production processes, in making technological improvements, and in avoiding duplication of research efforts. Even ideas for new products have been sparked by these reports.

Some 350 such reports are described each month in "U. S. Government Research Reports" (formerly the "Bibliography of Technical Reports") which is available from the U. S. Department of Commerce or any of its field offices at $6.00 a year.

The research covers nearly every field of industrial activity, including chemicals, plastics, paints, electrical machinery and electronics, foods, fuel and lubricants, instrumentation, leather, lumber, metals, minerals, paper, ordnance, physics, rubber, textiles, aeronautics, transportation, water supply, and other items.

"Should Your Child Be a Chemist?"

"Should Your Child Be A Chemist?" Dr. Irving Langmuir, renowned chemist and Nobel prize winner, answers this question in an advertisement sponsored by one of the nation's leading life insurance companies.

According to Dr. Langmuir, "the nation now employs 65,000 trained chemists—and badly needs more of them. The expansion of chemistry has been and continues to be so great that graduates leaving college today with degrees in chemistry are assured of jobs immediately."

Curiosity about things, and enthusiasm are two of the important tools with which the young chemist must be equipped, according to Dr. Langmuir. He points out that, "once the chemist's curiosity is focused on a problem, he will need enthusiasm to carry him forward to the answer. Granted these basic qualities, young men and women of many different talents and dispositions can find a suitable place in chemistry."

Dr. Langmuir explains that practically all the things that contribute to our well-being have a firm foundation in his field. In these modern times, "the field of the chemist and the chemical engineer is almost unlimited; it involves almost everything we do, and everything we touch."

The field of chemistry has become so wide-spread that many young chemists often find themselves far removed from their original studies and, "many of the chemical industries and their offshoots are beyond the ken of the nonscientist;

they often have trained chemists as executives and in their key office positions, their market research, their purchasing departments, and their publications."

Dr. Langmuir points out that the opportunities in chemistry today are boundless. He believes that, even though the opportunities for profit in his field are great, "many chemists find that their real reward is something more than money. When a man creates an insecticide that wipes out malaria, a fertilizer that bids fair to end starvation, a wonder drug that laughs at pneumonia —or when he makes any of the theoretical discoveries in pure science that make these practical applications possible—or when he builds the plant that brings these things to the public—then he knows what happiness means."

Technological Status of the U.S.A.

John T. Rettaliata, president of Illinois Institute of Technology, Chicago, prepared the following material in connection with the recent news announcement that President Eisenhower has appointed a cabinet committee to study the continuing shortage of young college-trained engineers and scientists.

Our government and defense officials are becoming concerned as a result of the report that nearly three times as many college-trained engineers and scientists are now being graduated each year in Russia as in the United States.

This situation may bring about corrections in military draft policies, and in some high school curriculum programs which have been keeping young engineers and scientists in short supply. President Eisenhower's appointment of a special cabinet committee to study the problem is a step in the right direction.

America's past engineering and scientific achievements are responsible, to a great degree, for its present strength, its wealth . . . and thus its international leadership . . . and the living comforts of its people. Its present ability to discourage enemy attack will be lost should an aggressor nation gain a comfortable margin in technological superiority.

Engineering educators are aware of two factors which are endangering the nation's technological superiority: One is the local draft board policy in some parts of the country of denying deferment to graduate students. The other is the spreading tendency in the high schools toward more general education programs which prepare fewer of their graduates to pursue scientific and engineering studies in college.

Generally, college students with satisfactory scholastic records are deferred until they complete their undergraduate studies. It is disturbing that those students who have the ability and desire to pursue advanced study are interrupted, frequently, by the requirement that they report for basic military training. This is serious because the real contributions toward fundamental research are made in the graduate field. The best candidates for future scientific leadership must have graduate training.

The inventory of basic scientific discovery is rapidly being depleted by the drain of technological progress. It is vital that this stockpile be constantly replenished lest we become a nation devoid of the means for future achievement. Educational institutions have always been the world's basic source of new knowledge; and, consequently, their graduate programs must remain in effect if this is to continue.

Selective service deferments should not be considered as granting privileges to a few people but rather as a means of improving the national security.

Because many graduate students are being drafted, in many instances their places in the laboratories of the nation's colleges are being filled by foreign students. This has the effect of this country training scientists for foreign countries instead of for its own people.

The national movement in high schools toward more general education will mean that more students will not have the required background in science and mathematics to pursue engineering and science programs later in college. This will further aggravate the shortage of engineers and scientists.

Actually, engineers and scientists constitute less than ½% of our population. Yet, we are relying on these people to continue the advance of our living standards, to create our military equipment, and, in general, be responsible for our national security.

In Russia, the engineering college program extends over a 5½-year period and contains very little study in the humanities or liberal arts field. Because of this specialization, the Russian graduate obtains more training in his field and, consequently, gets an education equivalent to that obtained by a master's degree student in this country. Furthermore, the Russians use forced placement according to the student's college major. Since this restricts occupational mobility, the areas where the need is greatest are filled more rapidly.

Furthermore, in order to increase the supply of engineers and scientists, Russia is training many women. It is estimated that women constitute about half of the total people in Russia's professional fields. It is known that, in 1940, women made up about 20% of the engineers; in this country, women engineers constitute a fraction of 1% of the total.

In this country, we are getting away from specialization in our engineering programs. We are including more humanities courses in our curricula. But, in a world of increasingly complex technology, where new developments are occurring at an expanded rate, it is becoming more difficult to prepare a student adequately at the undergraduate level. Consequently, to achieve the accomplishments desired, more students should be taking graduate courses. If they are not granted military deferments, this is not possible. We must make the decision as to whether we will have soldiers or scientists.

NSF Announces Science Grants

The National Science Foundation has announced 216 grants totaling about $2,650,000 for the support of basic research in the natural sciences, for conferences and studies on science, scientific information exchange, for scientific manpower, and for travel of American scientists to international scientific meetings.

This is the first group of awards to be made during fiscal year 1955 by the Foundation for the support of basic research and related matters. Since the beginning of the program in 1951, over 1100 such awards have been made, totaling about $11,141,000. In addition, the first grant, totaling $100,000, was made under a special appropriation for the International Geophysical Year.

Grants have been made to institutions and scientists in many of the 48 states, Italy, and Belgium. The research fields included are astronomy, chemistry, developmental biology, earth sciences, engineering sciences, environmental biology, genetic biology, mathematical sciences, molecular biology, physics, psychobiology, regulatory biology, and systematic biology.

Volumes Wanted

Society Headquarters needs copies of Vol. 92 (1947), 93 (1948), and 95 (1949) of the TRANSACTIONS.

Will anyone who has a copy he no longer needs please so inform the Managing Editor, Journal of The Electrochemical Society, 216 West 102 Street, New York 25, N. Y.

PERSONALS

JOHN C. KOSMOS has established a new metal finishing laboratory for conducting research in supplementary conversion coatings, conducting engineering service for metal finishing, and supplying shop personnel with their needs for maintenance and control of processes in electroplating and allied fields. Mr. Kosmos is the president and treasurer.

JOHN C. KOSMOS

C. A. SNAVELY was recently made assistant manager of chemical engineering at Battelle Memorial Institute, Columbus, Ohio.

MYRON B. DIGGIN is now assistant vice-president of Hanson-Van Winkle-Munning Company, Matawan, N. J.

W. A. LALANDE, JR., vice-president, research and development, Pennsylvania Salt Manufacturing Company, Philadelphia, has been named associate trustee of the University of Pennsylvania. A native Philadelphian, Dr. LaLande earned bachelor, master, and doctorate degrees at the University of Pennsylvania, and served as a member of its faculty from 1927 until 1937 when he accepted a research fellowship at the Swiss Federal Polytechnic Institute in Zurich. Dr. LaLande has been associated with Pennsalt since 1944, serving successively as director of research and manager of research and development.

ROBERT K. MCKECHNIE has been named as the new unit manager of a Materials Application Unit that has been established in the metallurgy department of the General Electric Research Laboratory, Schenectady, N. Y. Mr. McKechnie has been with GE since 1947, serving at Knolls Atomic Power Laboratory and with the Carboloy department before becoming a research associate in the materials and processes section of the GE Laboratory in 1952.

ROBERT K. MCKECHNIE

JOSEPH C. SCHUMACHER, until recently vice-president and director of research of Western Electrochemical Company, has joined American Potash & Chemical Corporation as director of research. In his new capacity, Mr. Schumacher will direct all research activities of the company and its subsidiaries under D. S. Dinsmoor, vice-president in charge of research and development. Mr. Schumacher will continue as a director of Western Electrochemical Company, located at Henderson, Nevada, in which American Potash & Chemical Corporation has a substantial interest.

MILTON STERN recently accepted a position as senior research assistant in the Metals Research Laboratories of the Electro Metallurgical Company, Niagara Falls, N. Y. Previously he was research associate at the Corrosion Laboratory, Massachusetts Institute of Technology, Cambridge.

SAMUEL S. SADTLER

Samuel S. Sadtler, first Secretary of The Electrochemical Society, died on November 2, 1954. He was 81 years old.

Mr. Sadtler attended Friends Central School from which he graduated in 1890. He attended the University of Pennsylvania for one year, leaving that school when his father, the late Samuel P. Sadtler, retired from the university. He then entered Massachusetts Institute of Technology from which he graduated in 1895 with a B.S. degree in chemistry. After graduation he went to work as a chemist in the Appraiser Stores, the U. S. Customs Service in New York.

SAMUEL S. SADTLER

In 1899 he joined the American Chemical Society, first of many chemical societies which he was to join and found during his busy career. At that time he helped found the Chemists' Club in New York. In 1902 he became the first Secretary of The Electrochemical Society. In 1903 he helped found, and became the first president of, the Meridian Club, a luncheon club in Philadelphia. In 1908 he joined the American Institute of Chemical Engineers while his father was its first president. He also belonged to the American Society for Testing Materials, the Engineers Club of Philadelphia, the Franklin Institute, and the Society of Chemical Industry of Great Britain. He was the second president of the Association of Consulting Chemists and Chemical Engineers and was an honorary charter member of the American Institute of Chemical Engineers. He was an active member for nearly twenty years of Rotary International.

In 1900 Mr. Sadtler left New York to return to Philadelphia to assist his father in the consulting laboratory which he had formed in 1891. As a consulting chemist, he at first assisted his father in numerous important patent lawsuits and other types of chemical litigation. The last important patent suit made a type of paving known as Amiesite available to all users.

S. S. Sadtler was an inventor who had over 30 U. S. patents. These included such subjects as nitro cellulose, asphalt paving, and nitro starch.

He wrote one book entitled "Chemistry of Familiar Things," published by J. B. Lippincott, Philadelphia, which went through nine editions. However, he was more editor than writer. In 1906 he edited the Chemical Abstract section of the *Journal of the American Chemical Society*; in 1907, Volume I, he was the section editor of *Chemical Abstracts*. He also became American editor of Allen's Commercial Organic Analysis, London.

His most important engineering project was the construction of a plant at Hopewell, Va., for the manufacture of rayon for the Tubize Chattillon Company according to the Chardinot process.

Mr. Sadtler is survived by his wife, Helena, and four children.

MEETINGS OF OTHER ORGANIZATIONS

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS (AIEE), High-frequency Measurements, Hotal Statler, Washington, D. C., Jan. 17–19.

AIEE, Committee on Technical Operations, 1955 Winter Meeting, General, Hotel Statler, New York, Jan. 31–Feb. 4.

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS, including Institute of Metals Division, Conrad Hilton Hotel, Chicago, Feb. 13–17.

TULSA SECTION, NATIONAL ASSOCIATION OF CORROSION ENGINEERS, Sixth Annual Corrosion Short Course for Pipeliners, Mayo Hotel, Feb. 16–18.

AIEE, Western Computer Conference, Hotel Statler, Los Angeles, March 1–3.

NATIONAL ASSOCIATION OF CORROSION ENGINEERS, Eleventh Annual Conference and Exhibition, Palmer House, Chicago, March 7–11.

AIEE, Electrical Utilization of Aluminum Conference, William Penn Hotel, Pittsburgh, March 15–17.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, Louisville, Ky., March 20–23.

AIEE, Materials Handling Conference, Hotel Cleveland, Cleveland, March 28–29.

AMERICAN SOCIETY FOR METALS, Western Metal Congress and Exposition, Los Angeles, March 28–April 1.

AMERICAN ASSOCIATION OF SPECTROGRAPHERS is planning its 6th Annual Conference in Chicago, May 6, on the subject "Industrial Applications of Spectroscopy." Contributed papers in the fields of Emission, X-Ray Fluorescence, or Absorption Spectroscopy as applied to industry are invited. *Abstracts must be submitted by March 1, 1955.* Please address all inquiries to: F. E. Stedman or E. E. Stilson, Co-Chairmen, Engineering Research Laboratory, Bendix Products Division, Bendix Aviation Corporation, 401 North Bendix Drive, South Bend 20, Ind.

NEW MEMBERS

In November 1954 the following were approved for membership in The Electrochemical Society by the Membership Qualifications Committee:

Active Members

ARTHUR HOIJORD ANDERSEN, Shawinigan Chemicals Ltd., 600 Dorchester St. West, Montreal, Quebec, Canada (Electrothermics and Metallurgy)

ERNST ARNOLD BLOCH, S.A. pour l'Industrie de l'Aluminium, Neuhausen am Rheinfall, Switzerland (Electrothermics and Metallurgy)

JOHN HAYES BRANNAN, National Carbon Co., P. O. Box 6087, Cleveland 1, Ohio (Industrial Electrolytic)

GEORGE MATTHEW BRUNNER, International Minerals and Chemical Corp., Royal Ave., Niagara Falls, N. Y (Industrial Electrolytic)

NORMAN RAE BRYANT, Burgess Battery Co., Mail add: 928 Jefferson Dr., Freeport, Ill. (Battery)

VERNON JACK CABLE, Stackpole Carbon Co., Mail add: 445 Maple St., St. Marys, Pa. (Industrial Electrolytic)

JAMES CARDELL, Raytheon Manufacturing Co., 55 Chapel St., Newton 58, Mass. (Electronics)

JOHN ALISTER COLGUHOUN, Shawinigan Chemicals Ltd., Mail add: 1442 George St., Shawinigan Falls, Quebec, Canada (Electrothermics and Metallurgy)

RICHARD ARTHUR DENTON, Optical Film Engineering Co., 2737 N. 6th St., Philadelphia, Pa. (Electrothermics and Metallurgy)

ROBERT M. GILL, Dewey and Almy Chemical Co., Cambridge 40, Mass. (Battery)

HARRY P. GREGOR, Polytechnic Institute of Brooklyn, 99 Livingston St., Brooklyn 1, N. Y. (Battery)

ROBERT WILLIAM HALL, Naval Ordnance Lab., Mail add: 906 N. Wayne St., Arlington, Va. (Electronics)

WAYNE H. KELLER, National Research Corp., Mail add: 101 Devonshire Rd., Waban 68, Mass. (Electrothermics and Metallurgy, Corrosion, Theoretical Electrochemistry)

ROBERT LANSING LOGAN, International Minerals and Chemical Corp., Mail add: 45 Arlington Rd., Williamsville 21, N. Y. (Industrial Electrolytic)

EDWIN STEELE MALKIN, National Carbon Co., Mail add: 748 Crescent Parkway, Westfield, N. J. (Industrial Electrolytic)

JOSEPH M. MANKO, Jones and Laughlin Steel Corp., Mail add: 309 Beaver Rd., Edgeworth, Pa., Sewickley P.O. (Corrosion, Electrodeposition)

ROBERT W. MARTEL, The New Jersey Zinc Co., Mail add: 248 Delaware Ave., Palmerton, Pa. (Electrodeposition, Theoretical Electrochemistry)

SANFORD J. NEUHAUS, The Aurilyte Process Co., Mail add: 100 Union St., Newark, N. J. (Electrodeposition)

ARTHUR L. OLENDER, Great Lakes Carbon Corp., Mail add: 2477 South Ave., Niagara Falls, N. Y. (Electrothermics and Metallurgy)

ROBERT L. PERKS, Shawinigan Chemicals Ltd., Shawinigan Falls, P.Q., Canada (Electrothermics and Metallurgy)

ERIC ARCHIBALD PLANCHE, Canadian Industries (1954) Ltd., Shawinigan Falls, Quebec, Canada (Industrial Electrolytic)

RHODES WILLIAMS POLLEYS, International Business Machines Corp., Mail add: 17 Horseshoe Rd., Hyde Park, N. Y. (Electrodeposition)

ROBERT HOLMS PUGH, General Dry Batteries Inc., Mail add: 5854 Amrap Dr., Cleveland 29, Parma Hts., Ohio (Battery)

PAUL L. RAYMOND, National Research Corp., Mail add: 17 Princeton Ave., Beverly, Mass. (Electrothermics and Metallurgy)

S. JOHN SANSONETTI, Reynolds Metals Co., 4th and Canal St., Richmond, Va. (Corrosion)

J. K. SARGENT, Jones and Laughlin

Steel Corp., Mail add: 639 Hall St., Aliquippa, Pa. (Corrosion, Electrodeposition)
RUDOLPH H. SCHINDLER, Metals Protection Co., Mail add: 125 Fairfax Rd., Pittsburgh 21, Pa. (Electrodeposition)
ROGER RUDOLPH TURK, Sylvania Electric Products Inc., Towanda, Pa. (Electrothermics and Metallurgy)
BORIS H. TYTELL, The Boston Naval Shipyard, Mail add: 14 Greendale Rd., Mattapan, Mass. (Corrosion)
JOHANNES MARTINUS ARNOLD VANDERHORST, Vanderhorst Corp. of America, Mail add: 103 Highland Pkwy., Olean, N. Y. (Electrodeposition)
PAUL A. WEIDLE, Ronson Corp. of Pa., Mail add: 90 Brown St., East Stroudsburg, Pa. (Electrodeposition)
DAVID ZUCKER, Titanium Alloy Mfg. Div., National Lead Co., Mail add: 1308 Garrett Ave., Niagara Falls, N. Y. (Electrothermics and Metallurgy)

Student Associate Member

BEN MATCHEN, Norton Co., Mail add: 1567 Ontario Ave., Niagara Falls, Ontario, Canada (Industrial Electrolytic)

Transfers to Active

SUDARSHAN DATTATRAYA GOKHALE, Institute of Physical Chemistry, 33 Wilhelm Strasse, Tubigen, W. Germany (Battery, Electrodeposition, Electro-Organic, Electrothermics and Metallurgy, Industrial Electrolytic, Theoretical Electrochemistry)
MILTON STERN, The Electro Metallurgical Co., Metals Research Lab., P. O. Box 580, Niagara Falls, N. Y. (Corrosion, Theoretical Electrochemistry)

BOOK REVIEW

ORGANIC COATING TECHNOLOGY, Volume 1, by Henry Fleming Payne. Published by John Wiley & Sons, Inc., New York, and Chapman & Hall Ltd., London, 1954. 674 pages, $10.00.

This is the first of two volumes designed to provide theoretical and practical information on organic coating technology for students and for new employees in the oil, resin pigment, and paint industries. The first chapter sets forth in graphic and easily understood form the fundamentals of film formation and structure. There is a splendid up-to-date description of the oils, resins, solvents, driers, and plasticizers employed in organic coatings. Film aging and deterioration are discussed and a chapter is devoted to test methods. Many resins and specific formulations well known in the trade literature are mentioned. Manufacture, composition, structure, and properties are stressed more than coating performance. The book contains a great amount of information and should be useful to the manufacturer, coating technologist, and the user of organic finishes.

R. M. BURNS

LETTER TO THE EDITOR

Terminology and Sign of Electrode Potentials

Dear Sir:

There appears to be general agreement[1] that the measured voltage E of an electrolytic cell should be taken to be a positive number. For the discharge (spontaneous) cell reaction, therefore, the increase in free energy for a reversible cell at constant T and P is:

$${}_d(\Delta F) = -n\mathbf{F}E \qquad \text{(I)}$$

and for the charge (reverse) reaction:

$${}_c(\Delta F) = +n\mathbf{F}E \qquad \text{(II)}$$

Since the positive cell voltage is the difference in potential between the two electrodes, one must write, assuming no junction potentials or other spurious voltages,

$$E = E_p - E_n \qquad \text{(III)}$$

where E_p is the potential of the more positive electrode and E_n that of the more negative electrode. It is necessary to use a nonthermodynamic argument to decide which electrode should be assigned the more positive potential, because thermodynamics deals only with the electrical work done by a complete cell.

Textbooks of thermodynamics or electrochemistry follow Lewis and Randall[2] in stating that, after one assigns the value $E^0 = +0.76$ v to the (oxidation) electrode reaction

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{++} + 2e, \qquad \text{(IV)}$$

it is a thermodynamic requirement that $E^0 = -0.76$ v for the reverse (reduction) reaction. The main point of this communication is to emphasize that the sign reversal is a nonthermodynamic convention. Moreover, it tends to be a misleading convention in terms of laboratory measurements.

This may be illustrated by Fig. 1, which represents a potentiometric measurement of the voltage of the standard zinc-hydrogen cell. Let us first select the sign of the potential, for the present purpose, by turning to electrostatics and utilizing the following electrical axiom: if electrons flow along a conductor from A to B, the electrical potential at A is more negative than that at B. Thus, with the zinc electrode connected to n in Fig. 1, one would find no galvanometer deflection when the hydrogen electrode is connected to a point p which is at a potential 0.76 v more positive than that at n, i.e., $E^0_{\mathrm{Zn}} = -0.76$ v on the hydrogen scale (the so-called European convention).

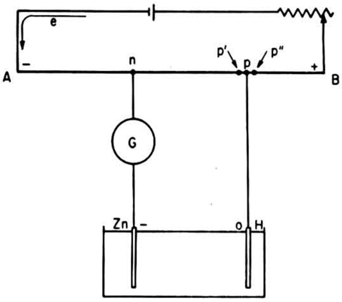

FIG. 1

When the connection to p is moved slightly toward n, to p', the cell discharges at a minute rate and the zinc electrode is the more negative by an amount just greater than $|\, p'n \,|$, i.e., $E^0_{\mathrm{Zn}} = -0.76$ v. When the connection is moved to p'', the reverse cell reaction takes place at a minute rate and the zinc electrode is the more negative by an amount slightly less than $|\, p''n \,|$, i.e., $E^0_{\mathrm{Zn}} = -0.76$ v again. It is a laboratory observation, therefore, that the sign of a reversible electrode potential does not reverse when the electrode reaction is reversed.

This is readily shown to be consistent with thermodynamics. Taking as an example the same zinc-hydrogen cell, one writes from equation (III):

$$E^0 = E^0_{\mathrm{H}} - E^0_{\mathrm{Zn}} = -E^0_{\mathrm{Zn}} \qquad \text{(V)}$$

whether the cell is being charged or

[1] W. M. LATIMER, *J. Am. Chem. Soc.*, **76**, 1200 (1954).

[2] G. N. LEWIS AND M. RANDALL, "Thermodynamics," McGraw-Hill Book Co., Inc., New York (1923).

discharged. For the discharge reaction one obtains from (I) and (V)

$${}_d(\Delta F^0) = {}_d(\Delta F^0)_{\mathrm{H}} + {}_d(\Delta F^0)_{\mathrm{Zn}} = {}_d(\Delta F^0)_{\mathrm{Zn}} = +2\mathbf{F}E^0_{\mathrm{Zn}} \qquad \text{(VI)}$$

and similarly for the charge reaction

$${}_c(\Delta F^0)_{\mathrm{Zn}} = -2\mathbf{F}E^0_{\mathrm{Zn}} \qquad \text{(VII)}$$

Thus the thermodynamic requirement, that the sign of the free energy be reversed when the reaction is reversed, is satisfied.

There would be greater simplicity and consistency if the terms "oxidation potential" and "reduction potential," as well as the sign reversal associated with them, would fall into disuse and leave just *electrode potential* (on the hydrogen scale).

Sidney Barnartt
Chemical Department
Westinghouse Research Laboratories
East Pittsburgh, Pa.

RECENT PATENTS

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

September 28, 1954

Lilliendahl, W. C., Wroughton, D., Nagy, R., and Marden, J. W., 2,690,421, Electrolytic Production of Uranium Powder
Szekely, G., 2,690,422, Electroplating of Germanium
Moschel, W., and Muller, W., 2,690,423, Photochemically Produced Copolymers
Hassell, E. J., 2,690,424, Apparatus for Reduction of Heavy Edge Coating in Electroplating
Duckwall, R. H., 2,690,462, Thermocouple
Clevett, M. L., Jr., and Fiske, D. L., 2,690,463, Thermoelectric Power Cell
Harris, J. E., 2,690,464, Storage Battery Grid
Broder, J. D., 2,690,465, Solid Ion Electrolyte Battery
Kendall, T. L., and Heritage, J. E., 2,690,466, Submersible Vent Cap for Storage Batteries
Kendall, T. L., 2,690,467, Vent Plug
Haubursin, R., 2,690,544, Battery Tester

October 5, 1954

Chubb, M. F., Reissue 23,883, Cuprous Chloride Electrodes
Gillmeister, F. W., 2,690,982, Coated Electrode
Brown, H., 2,690,996, Electroplating of Nickel
Jernstedt, G. W., 2,690,997, Electrodeposition of Copper
Wolff, J. A., 2,691,056, Thermoelectric Device Having Opposing Thermoelectric Generator
Wooding, W. M., 2,691,135, Automatic Instrument for Determining Permeability of Porous Dielectrics
De Waard, R., 2,691,136, Automatic Circuit-Making Liquid Applicator
Parsons, C. H., and Perme, R. J., 2,691,144, Electroforming Apparatus for Rectifier Disks

October 12, 1954

Lark-Horovitz, K., and Whaley, R. M., 2,691,577, Alloys and Rectifiers Made Thereof
Butler, K. H., and Homer, H. H., 2,691,601, Phosphor Treatment
Johnson, R. E., 2,691,627, Method of Producing Decorated Aluminum Articles
Aannerud, S. A., 2,691,628, Electrode Structures
Arbeit, P., and LaBurthe, P., 2,691,689, Glass Tank Furnace and Method of Operating the Same
Poch, S., and Lewis, J. C., Jr., 2,691,690, Thermocouple Element Composition

October 19, 1954

Jenkins, A., and Peter, L. H., 2,692,212, Manufacture of Dry Surface Contact Rectifiers
✓ Ruben, S., 2,692,215, Alkaline Dry Cell
Clancy, R. F., 2,692,228, Electrolytic Recording Paper
De Piolenc, G., and Russell, R. G., 2,692,296, Glass Melting Furnace
Ouweltjes, J. L., 2,692,349, Low-Pressure Mercury Vapor Discharge Lamp

October 26, 1954

Halm, E., 2,692,817, Process for the Production of Carbon Disulfide
Safranek, W. H., Schickner, W. C., and Faust, C. L., 2,692,850, Aluminum Electroforming
Burrows, C. F., 2,692,851, Method of Forming Hard, Abrasion-Resistant Coatings on Aluminum and Aluminum Alloys
Burrows, C. F., 2,692,852, Method of Producing Hard, Abrasion-Resistant Coatings on Aluminum and Aluminum Alloys
Gamble, T. S., 2,692,853, Process and Composition for Electropolishing Stainless Iron and Steel
✓ Strauss, H. J., 2,692,904, Growth Inhibitor for Battery Electrodes
✓ Fischbach, A., and Mandel, H. J., 2,692,905, Battery Design for Guided Missile Applications
✓ Morgan, W. T., 2,692,906, Storage Battery
✓ Wallace, C. C., 2,692,907, Storage Battery Seal

ANNOUNCEMENTS FROM PUBLISHERS

Bibliography of Books and Published Reports on Gas Turbines, Jet Propulsion and Rocket Power Plants by E. F. Frock and Carl Halpern. Supplement to National Bureau of Standards Circular 509 issued in 1951. Published by Government Printing Office, Washington 25, D. C. 110 pages, 50¢.

Methods for Emission Spectrochemical Analysis. ASTM Committee E-2. Published by American Society for Testing Materials, 1916 Race Street, Philadelphia 3, Pa., 1953. 309 pages, paper bound, $4.50; cloth bound, $5.15.

Index to the Literature on Spectrochemical Analysis, Part III, 1946–1950, by Bourdon F. Scribner and William F. Meggers. ASTM Special Technical Publication No. 41-C. Published by American Society for Testing Materials, Philadelphia, 1954. 226 pages, $4.50, paper cover.

The third in this series of bibliographical surveys of the literature of spectrochemical analysis contains 1264 references listed chronologically by years and alphabetically by author within each year. Detailed subject index and an author index included.

Analytical Index of Chemical Engineering Publications, Patents and Reports, Chemical Engineering Report No. 10, by the Staff of the Office of Chemical Engineering, Tennessee Valley Authority. Published by the U. S. Government Printing Office, Washington, 1954. 192 plus vi pages, 55¢, paper cover.

A catalogue—by subject—of publications, patents, and internal reports covering a large part of TVA's chemical engineering activities since 1933. The range of subject matter is very broad and includes much of elec-

(Continued on page 20C)

Society Prizes and Awards

The Edward Goodrich Acheson Medal and Prize

The Edward Goodrich Acheson Gold Medal and $1,000 Prize were founded by Dr. Acheson in August 1928.

The award is made once every two years (first award at the Fall Meeting, 1929) to the person who shall have made a distinguished "contribution to the advancement of any of the objects, purposes, or activities . . . of the Society. Such contribution may consist of but shall not be limited to (*a*) a discovery pertaining to electrochemistry, electrometallurgy, or electrothermics, (*b*) an invention of a plan, process or device, or research evidence by a paper embodying information, useful, valuable, or significant in the theory or practice of electrochemistry, electrometallurgy, or electrothermics, and/or (*c*) distinguished services rendered to the Society or its successor."

The award is made without distinction on account of sex, citizenship, race, or residence. See *Trans. Electrochem. Soc.*, **54,** 6 (1928).

The Palladium Medal

The Palladium Medal of The Electrochemical Society was founded in 1950. The source of funds for the establishment of the medal is the royalties derived from sales of the *Corrosion Handbook* which was sponsored and largely written by members active in the Corrosion Division of the Society. Dr. H. H. Uhlig served as Editor-in-Chief.

The award of the medal is to be made every two years to a scientist, in recognition of original and outstanding contributions to the knowledge of corrosion in one or more of the following fields: the theory of corrosion or corrosion control, electrode potentials, properties of electrolytes, electrode reactions, and the surface properties of metals. The jury for the selection of the medalist is appointed by the Board of Directors of the Society and consists of three members, including one member from the Corrosion Division and one from the Theoretical Division, both of whom are active in their respective fields. See *J. Electrochem. Soc.*, **98,** 95C (1951).

The Joseph W. Richards Memorial Lectureship

Dr. Joseph William Richards was one of the founders of The Electrochemical Society, and its first President. He was Secretary and Editor of the Society's TRANSACTIONS from 1904 to 1921. His very active and untiring interest in the Society and in the science and art of electrochemistry reflected itself in the rapid growth of the Society and of the electrochemical industry throughout the world. From the very start, Dr. Richards fostered the international spirit.

The Joseph W. Richards Memorial Lectureship was established in 1929 by a group of friends and admirers of Dr. Richards. The interest of the fund is used to meet the expenses incurred by inviting and entertaining distinguished scientists. See *Trans. Electrochem. Soc.*, **57,** 30 (1930).

The Electrochemical Society Prize to Young Authors

An annual prize of one hundred dollars was established by the Board of Directors in July 1928. The prize is awarded to the author of the best paper printed in the yearly volume of the JOURNAL of the Society. The judges to pass upon the merits of the paper are the Chairman of the Publication Committee, the Secretary of the Society, and three members of the Society, and two alternates, selected by the Chairman of the Publication Committee, the Committee being at liberty to invite the opinion of members not on the Committee.

The prize is open to students and graduates under thirty-one years of age of any technical school, college, or university, no matter where located. See *Trans. Electrochem. Soc.*, **55,** 22 (1929); **92,** viii (1947).

Francis Mills Turner Award, Sponsored by the Reinhold Publishing Corporation

For several years, Francis Mills Turner personally offered an annual prize consisting of $50.00 worth of scientific and technical books published by the Reinhold Publishing Corpora-

Honorary Members of the Society

CHARLES F. CHANDLER,* New York, N. Y.	Volume 35 (1919)
EDGAR F. SMITH,* Philadelphia, Pa.	Volume 35 (1919)
CARL HERING,* Philadelphia, Pa.	Volume 41 (1922)
EDWARD G. ACHESON,* Niagara Falls, N. Y.	Volume 43 (1923)
WILDER D. BANCROFT,* Ithaca, N. Y.	Volume 47 (1925)
EDWARD WESTON,* Montclair, N. J.	Volume 50 (1926)
THOMAS A. EDISON,* Orange, N. J.	Volume 54 (1928)
W. LASH MILLER,* Toronto, Canada	Volume 55 (1929)
EDWARD DEAN ADAMS,* New York, N. Y.	Volume 57 (1930)
CHARLES F. BURGESS,* Chicago, Ill.	Volume 62 (1932)
FREDERICK MARK BECKET,* New York, N. Y.	Volume 66 (1934)
L. H. BAEKELAND,* New York, N. Y.	Volume 69 (1936)
ROBERT A. WITHERSPOON,* Montreal, Canada	Volume 78 (1940)
ARCHER E. WHEELER, New York, N. Y.	Volume 80 (1941)
W. R. WHITNEY, Schenectady, N. Y.	Volume 85 (1944)
PAUL J. KRUESI, Chattanooga, Tenn.	Volume 85 (1944)
COLIN G. FINK,* New York, N. Y.	Volume 89 (1946)
JOHN W. MARDEN, Bloomfield, N. J.	Volume 91 (1947)
WILLIAM BLUM, Washington, D. C.	Volume 100 (1953)

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* Deceased

tion. At the time of his demise, the Reinhold Publishing Corporation established the "Francis Mills Turner Memorial Award, Sponsored by the Reinhold Publishing Corporation," consisting of $100.00 worth of scientific and technical books to be given each year to an author under 31 years of age. This revision was gratefully accepted by the Board of Directors at the Society convention held in Philadelphia, May 4 to 8, 1952. See *J. Electrochem. Soc.*, **99,** 162*C* (1952).

Consolidated Fellowship Fund

Due to the deterioration of the Weston Fellowship funds, the Board of Directors on October 26, 1952 established a Consolidated Fellowship Fund from the accumulated earnings of the Weston Fellowship Fund, the entire Roeber Research Fund, the excess earnings of the Acheson Fund, and the $1000 returned by John W. Marden (Acheson Award) at the Montreal Meeting. This fund will be accumulated until such time as the Society has available sufficient yearly income from this source to justify offering a fellowship, at which time the Society again will be in a position to sponsor graduate studies in electrochemistry.

Former recipients of the Acheson Medal and Weston Fellowship are listed below.

Prize Essay Contest

The Electrochemical Society sponsors an essay contest, which is open to undergraduate and graduate students, on a selected subject. Two prizes are awarded for the two best essays submitted: first prize is $100, plus a one-year subscription to the Journal; second prize is $50, plus a one-year subscription to the Journal.

Prizes for the contest are financed by royalties from the sale of the "Corrosion Handbook," a widely used technical publication sponsored by the Corrosion Division and published by John Wiley & Sons, Inc., in 1948. See *J. Electrochem. Soc.*, **100,** 68*C*, 282*C* (1953).

Winners of Society Prizes and Awards

Acheson Medalists

Edward G. Acheson*—Artificial Graphite and Carborundum—**56,** 7 (1929).

Edwin F. Northrup*—Induction Furnaces—**60,** 8 (1931).

Colin G. Fink*—Electrochemistry—**64,** 2 (1933).

Frank J. Tone*—Electrothermics—**68,** 2, 8 (1935).

Frederick M. Becket*—Electrothermics—**72,** 3 (1937).

Francis C. Frary—Electrometallurgy—**76,** 4 (1939).

Charles F. Burgess*—Electrochemistry—**82,** 3 (1942).

William Blum—Electrodeposition—**86,** 4 (1944).

H. Jermain Creighton—Electro-Organic Chemistry—**90,** 5 (1946).

Duncan A. MacInnes—Electrochemistry—**94,** 4*P* (1948).

George W. Vinal—Batteries—**97,** 231*C* (1950); **98,** 11*C* (1951).

John W. Marden—Electronics—**100,** 37*C* (1953).

George W. Heise—Batteries—**101,** 291*C* (1954).

Weston Fellowship Holders

Edward B. Sanigar—"The Titration of Potassium Cyanide and of Free Cyanide in Silver-Plating Solutions by Means of Silver Nitrate"—**58,** 435 (1930); "Electrodeposition of Silver from Sulfate, Nitrate, Fluoborate and Fluoride Solutions"—**59,** 307 (1931).

Karl Sollner—"An Experimental Study of Negative Osmosis. Part I"; "Experimental Verification of a New Theory Concerning the Mechanism of Anomalous Osmosis. Part II"—**61,** 477, 487 (1932).

Marlin E. Fogle—"A Study of Cuprous Oxide Solid Photoelectric Cells"—**66,** 271 (1934).

Robert D. Blue—"Electrodeposition of Aluminum from Non-Aqueous Solutions"—**65,** 339 (1934).

Pierre A. Jacquet—"Effect of Colloids on Electrodeposition"—**65,** 21 (1934).

Myron A. Coler—"Electrolytic Processes in the Magnetic Field"—**72,** 247 (1937).

Henry B. Linford—"The Effect of the Speed of Rotation on the Electrode Potentials of Copper and Zinc"—**72,** 461 (1937).

Garth L. Putnam—**71,** 26 (1937).

Vittorio de Nora—**73,** 39 (1938).

Waldemar P. Ruemmler—**75,** 52 (1939); **77,** 50 (1940).

Rodney E. Black—**79,** 44 (1941).

William E. Roake—**81,** 46 (1942).

Robert D. Misch—**93,** 14*P* (1948).

Massoud T. Simnad—**94,** 3*N* (1948)†; **97,** 161*C* (1950).

Joseph W. Richards Memorial Lecturers

John A. Mathews,* Vice-President and Director of Research, Crucible Steel Company, New York, N. Y. "The Electric Furnace and the Alloy Age," **61,** 143 (1932).

R. S. Hutton, Goldsmiths' Professor of Metallurgy, University of Cambridge, England. "Faraday and His Electrochemical Researches," **64,** 13 (1933).

W. S. Landis,* Vice-President and Director, American Cyanamid Company, New York, N. Y. "Joseph W. Richards, The Teacher—The Industry," **66,** 6 (1934).

Karl K. Darrow, Physicist, Bell Telephone Laboratories, New York, N. Y. "Electricity in Gases," **69,** 67 (1936).

Charles H. Herty,* Director, Herty Foundation Laboratory, Savannah, Ga. "The Utilization of Southern Pine," **73,** 50 (1938).

Bradley Stoughton, Dean of Engineering, Lehigh University, Bethlehem, Pa. "Modern Marvels of Electrometallurgy," **76,** 29 (1939).

Vladimir K. Zworykin, Associate Director of RCA Research Laboratories, Camden, N. J. "The Electron Microscope," **80,** 14 (1941).

B. D. Saklatwalla,* Metallurgical Consultant, Pittsburgh, Pa. "Thermal Reactions in Ferro-Alloy Metallurgy, the Basis of Alloy Steel Development," **84,** 13 (1943).

Stewart J. Lloyd, Professor of Chemical Engineering, University of Alabama, University, Ala. "Freedom in Science," **89,** 9 (1946).

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* Deceased.

† *J. Electrochem. Soc.*

* Deceased.

Oliver W. Storey, Consultant, Burgess Battery Company, Chicago, Ill. "Research in Industry—Is Government Antagonistic to It?" **96,** 3*P* (1949); **97,** 9*C* (1950).

J. O'M. Bockris, Lecturer, Department of Inorganic and Physical Chemistry, Imperial College of Science and Technology, London University, London, England. "Overpotential," **98,** 153*C* (1951).

Palladium Medalists

Carl Wagner, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass. "The Electrochemistry of Ionic Crystals," **99,** 346*C* (1952).

Nathaniel Howell Furman, Chairman, Department of Chemistry, Princeton University, Princeton, N. J. "Coulometry—Related Phenomena of Electrolysis and Current-Sweep Polarography," **101,** 19*C* (1954).

Winners of Young Authors' Prize

William C. Gardiner—"Hydrolysis of Mercurous Sulfate by Cadmium Sulfate Solution in the Weston Normal Cell"; "Oxidation of the Depolarizer in Preparing Standard Cells"; "Crystalline Mercurous Sulfate and the Weston Normal Cell"—**56,** 111 (1929).

Dwight K. Alpern—"Engineering Development of Photovoltaic Cells"—**58,** 275 (1930).

Frank L. Jones—"Electrodeposition of Tungsten from Aqueous Solutions"—**59,** 461 (1931).

F. W. Godsey, Jr.—"Alternating Current Capacities of Electrolytic Condensers"; and "Potential Gradients in Anodic Films"—**61,** 515, 549 (1932).

B. L. Bailey—"Hardness Values for Electrochemical Products"—**63,** 369 (1933).

Joseph R. Heard, Jr.—"Electro-Organic Oxidations in Concentrated Aqueous Organic Salt Solutions"—**65,** 301 (1934).

Upton B. Thomas, Jr.—"Electrochemical Behavior of Lead, Lead-Antimony and Lead-Calcium Alloys in Storage Cells"—**68,** 293 (1935).

W. A. Johnson—"Studies of Overvoltage: Effect of Fusion of the Cathode and Effect of Temperature on Gas Polarization"—**70,** 259 (1936).

R. Spencer Soanes—"Potential Distribution in High Current Carbon Arcs in Air"—**72,** 281 (1937).

N. B. Nichols—"The Cathode Ray Oscillograph Applied to the Dropping Mercury Electrode"—**73,** 193 (1938).

G. A. Moore—"Comportment of Palladium-Hydrogen System toward Alternating Electric Current"—**75,** 237 (1939).

J. S. Mackay—"Photoelectric Cells Sensitive to Long Wave Length Radiation: The Bismuth Sulfide Cell"—**77,** 299 (1940).

Edward Adler—"Photovoltaic Effect"; "Semi-Conductor Photocells and Rectifiers"—**79,** 367, 377 (1941).

Sidney Speil—"Electrophoretic Dewatering of Clay"—**81,** 119 (1942).

Walter G. Berl—"A Reversible Oxygen Electrode"—**83,** 253 (1943).

John P. Coyle—"The Extraction of Indium from Complex Lead-Tin Alloys"—**85,** 223 (1944).

Austin E. Hardy—"The Photoconductivity of Zinc-Cadmium Sulfide as Measured with the Cathode-Ray Oscillograph"—**87,** 355 (1945).

Norman A. Nielsen—"Passivation of Stainless Steels"—**89,** 167 (1946).

Henry Leidheiser, Jr.—"The Influence of Crystal Face on the Electrochemical Properties of a Single Crystal of Copper"—**91,** 95 (1947).

Michael A. Streicher—"The Dissolution of Aluminum in Sodium Hydroxide Solutions" — **93,** 285 (1948).

J. C. Griess, Jr.—"The Electrodeposition Behavior of Traces of Silver"—**95,** 33 (1949).

George W. Murphy—"The Separation of Simple Electrolytes in Solution by an Electro-Gravitational Method"—**97,** 405 (1950).

John T. Byrne—"Critical Interpretation of Electrodeposition Studies Involving Traces of Elements"—**98,** 457 (1951).

W. E. Kuhn—"Production of Titanium Ingots by Melting Sponge Metal in Small Inert-Atmosphere Arc Furnaces"; "Development of Graphite Electrodes and Study of Heat Losses with Different Electrodes in the Single Electrode Inert-Atmosphere Arc Furnace"—**99,** 89, 97 (1952).

J. Halpern—"Kinetics of the Dissolution of Copper in Aqueous Ammonia"—**100,** 421 (1953).

Winners of Turner Book Prize

Sidney Speil—"Electrophoretic Dewatering of Clay"—**81,** 119 (1942).

Walter G. Berl—"A Reversible Oxygen Electrode"—**83,** 253 (1943).

John P. Coyle—"The Extraction of Indium from Complex Lead-Tin Alloys"—**85,** 223 (1944).

James T. Waber—"Stress Corrosion Cracking of Mild Steel"—**87,** 209 (1945).

Burke Cartwright—"Electrolysis of Manganese into a Metal Cathode from Suspensions of Manganese Oxide and Carbon in Molten Manganous Chloride"—**89,** 373 (1946).

Austin E. Hardy—"A Combination Phosphorometer and Spectroradiometer for Luminescent Materials"—**91,** 221 (1947).

Michael A. Streicher—"The Dissolution of Aluminum in Sodium Hydroxide Solutions"—**93,** 285 (1948).

Ralph F. Hoeckelman—"Salt-Bath Chromizing"—**96,** 262 (1949).

Paul Delahay—Parts I and II of the paper "A Polarographic Method for the Indirect Determination of Polarization Curves for Oxygen Reduction on Various Metals"—**97,** 198, 205 (1950).

Kurt H. Stern and Charles C. Templeton—"The Electrical Conductance of Solutions of Cobalt (II) Nitrate Hexahydrate in Acetophenone at 25°C"—**97,** 443 (1951).

P. T. Gilbert—"The Nature of Zinc Corrosion Products"—**99,** 16 (1952).

Robert B. Holden—"The Hot-Wire Process for Zirconium" (co-author, Bernard Kopelman) — **100,** 120 (1953).

Announcements From Publishers

(Continued from page 17C)

trochemical interest from the electric-furnace production of phosphorus to corrosion.

Gmelin's Handbook of Inorganic Chemistry. Five volumes of the 8th edition of this famous work have become available. These are edited by the Gmelin Institute under the direction of E. H. E. Pietsch, and published by Verlag Chemie, GmbH., Weinheim/Bergstr., West Germany. They may be obtained in the United States through Walter J. Johnson, Inc., 125 E. 23rd St., New York 10, N. Y., and Stechert-Hafner, Inc., 31 E. 10th St., New York 3, N. Y. The individual volumes are as follows:

Sulfur. System No. 9, Section A 3,

1953. XVI plus 252 pages, 54 graphs. $34.00. This is devoted to the physics and chemistry of elementary sulfur.

Selenium. System No. 10, Part A, Section 3, 1953. XVII plus 184 pages, 158 graphs. $26.64. This volume is devoted to the selenium rectifier and photocell and contains considerable new information obtained in World War II developments.

Boron. System No. 13, Supplement Volume, 1954. VII plus 253 pages, 28 graphs. In wrappers $33.60, cloth bound $34.80. This is the first complete and modern monograph on boron and its compounds.

Gold. System No. 62, Part 2, 1954. V plus 306 pages, 20 graphs. $40.32. This is the second part of the Gold volume, the first having appeared in 1950. It has to do with the occurrence, manufacture, formation, and preparation of special modifications in the pure state and the surface treatment of gold and gold alloys.

Gold. System No. 62, Part 3, 1954. XXI plus 558 pages, 201 graphs. $74.88. This volume completes the gold series and covers the properties and physiological behavior and the general reaction of gold salts.

HISTORY OF AMERICAN INDUSTRIAL SCIENCE by Courtney R. Hall. Published by Library Publishers, New York, 1954. 453 plus xix pages, $4.95.

A history of the relation between science and industry in this country from the earliest days of the Industrial Revolution to the present time, based on information supplied by sixty of the leading American corporations and written by an historian, shows the development of what is perhaps the chief characteristic of the American nation: its industrial "know-how."

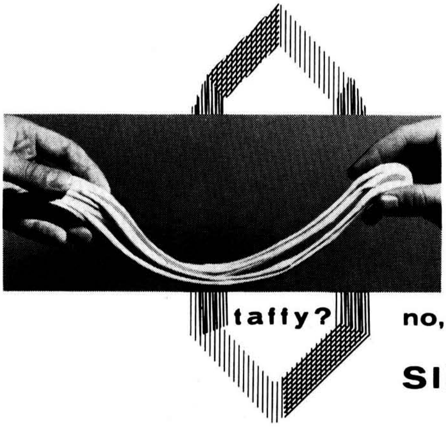
LITERATURE FROM INDUSTRY

MOLYBDENUM CHEMISTRY. Publication of a new series of molybdenum chemical data bulletins was recently announced. These bulletins are designed to provide, in concise form, authoritative data on the properties of molybdenum compounds. Previously such data were often difficult to find in the literature and hard to evaluate. The first bulletin in the series is entitled "Properties of Molybdic Oxide." It presents selected values for the physical properties of this basic molybdenum compound and a review of its chemical properties. Molybdic oxide is used as a catalyst, an intermediate for the production of molybdates and metallic molybdenum, an alloying agent for steel, and a constituent of special ceramics. Climax Molybdenum Co. P-260

TECHNIC PRICE FOLDER. Soluble precious metals available for electroplating are listed, along with a statement on precious metal electroplating with scientific accuracy, in a new price card. Previously, the growing importance of precious metal electroplating throughout industry has induced Technic Inc. to publish technical data, much of it original, on gold and rhodium solutions for electroplating. The new price list complements this material with specific data and prices which will enable engineers and purchasing agents to compute manufacturing costs. The new price list is in the form of a card folded to convenient pocket size, imprinted on heavy stock to permit constant reference. Technic Inc. P-261

CHROMATE FINISHING. A comprehensive file of technical literature on Iridite Chromate Conversion Coatings for prevention of corrosion and paint-base treatment of nonferrous metals has been issued. The brochure consists of a handy standard-size file folder with 8 dividers classifying data by (*a*) general information, (*b*) metal to be treated, and (*c*) finishing processes. In addition to the basic file, detailed "Technical Information" sheets for insertion in these sections offer general technical and government specification data of value to finishers, and specific operating instructions for individual processes. Allied Research Products, Inc. P-262

"PHYSICAL PROPERTIES OF SYNTHETIC ORGANIC CHEMICALS." 1955 edition of the booklet has been issued by Carbide and Carbon. In 24 pages, this edition presents the latest data



on more than 350 organic chemicals. It features 46 new products available. The booklet is prepared annually as a handy guide for chemists, engineers, purchasing agents, and laboratory workers. For easy reference, the chemicals are arranged by family groups with condensed application data. Physical properties are given in tabular form. An alphabetical index is included for the convenience of the user. Carbide and Carbon Chemicals Co. P-263

Electroplated Palladium and Platinum. An authoritative data sheet on electroplated palladium and electroplated platinum has been issued. For each metal, the compilation describes physical properties, from atomic weight to reflectivity, and electrical properties, from resistivity to specific magnetic susceptibility. Corrosion resistance is also detailed, along with hardness electroplated, electroplating specifications, and thickness requirements. Cost of electroplating per square foot is estimated. Although the sheet comprises complete information on both electroplated palladium and platinum, it is organized in convenient form to make all details available at a glance. Technic Inc. P-264

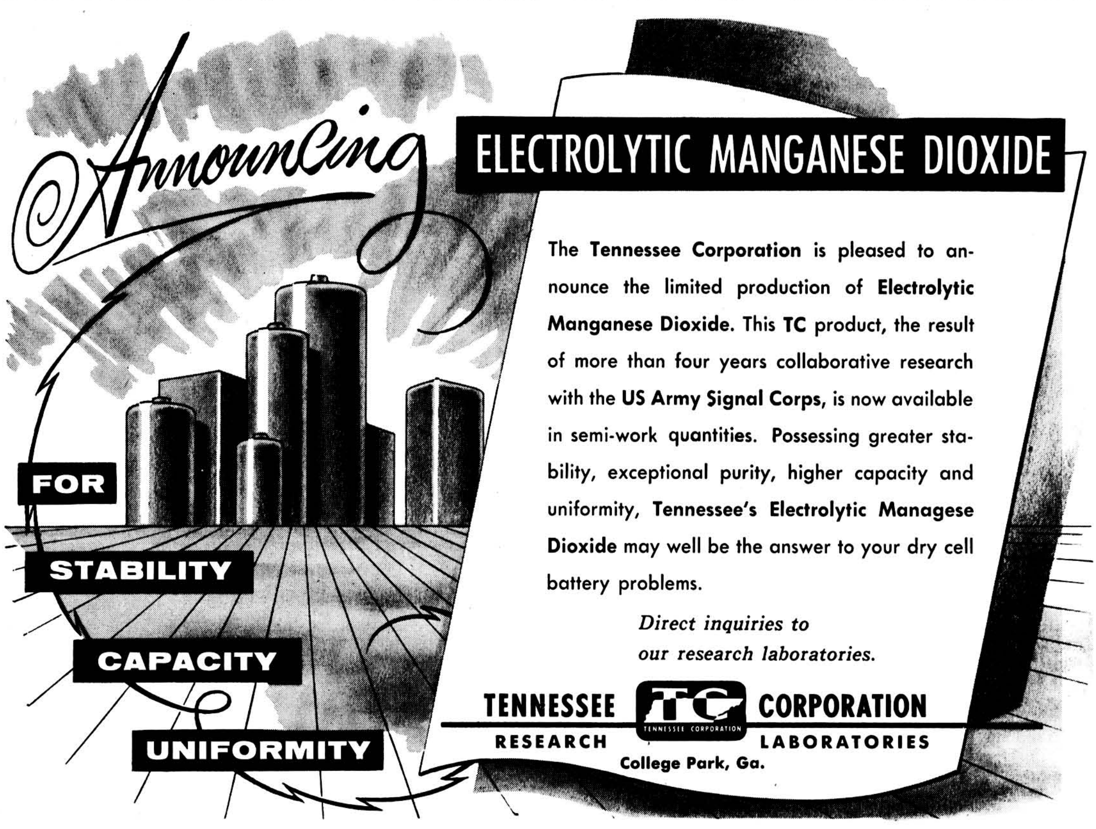
"The Laboratory," Vol. 24, No. 1, celebrates the 100th anniversary of the birth of Paul Ehrlich with a feature story on the rise of chemotherapy. Among the new instruments announced in the same issue is the Fisher Amperometric Titrimeter, which permits analysis in solutions as dilute as $0.000001N$, with a platinum micro-electrode that is 18 to 20 times more sensitive than the dropping mercury electrode. Among the new literature announced is the fully revised, completely rewritten *Fisher/Tag Manual for Inspectors of Petroleum*, the 28th edition of a universally used book. Fisher Scientific Co. P-265

NEW PRODUCTS

Enclosed Gyro Degreasers. Entirely new designs of automatic, totally enclosed "gyro" degreasers, including an adaptation of the gyro or "ferris wheel" principle to incorporate rotating work baskets, have been announced. The degreasers are ideally suited for cleaning small parts, both ferrous and nonferrous, in basket loads. The totally enclosed design reduces solvent consumption, prevents the disturbance of vapors by cross drafts in the plant, and keeps the operating zone entirely free from solvent fumes even when the door is open. Detrex Corp. N-133

Amperometric Titrimeter. Amperometric titration is now at the disposal of any laboratory which adds the new Amperometric accessory to its Elecdropode, a widely used, low-priced manual polarograph introduced by Fisher. With the Amperometric Titrimeter, traces of such impurities as cadmium, copper, zinc, lead, antimony, or arsenic can be "picked out" in complex alloys, and essential components such as chromium, cobalt, nickel, man-

(Continued on page 24C)



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L. Charat Ram and K. Rajagopal

New Products

(*Continued from page 22C*)

ganese, vanadium, or titanium assayed with precision . . . often in solutions as dilute as 0.000001*N*. Chloride and bromide can be isolated from other halides, and cyanide, phosphate, chromate, sulfate, and many other ions found by titration where other methods fail. Numerous organic compounds can be determined directly. Fisher Scientific Co. N-134

SMALLEST COMMERCIAL THERMISTOR. A new type thermistor combining the high speed response of the smallest commercially available model with extreme stability at high operating temperatures has been developed. The thermistor, TCA type L 118, is a tiny, glass-coated ceramic element less than 18 thousandths of an inch in diameter with 1 mil diameter platinum alloy leads. Thermistors of this size previously available were rated for a maximum continuous temperature of 150°C. The new type is rated at 300°C where it is extremely stable, and is useful even to 400°C with good stability. Thermistor Corp. of America N-135

NEW L&N INSTRUMENTS. Two new instrument lines—termed Speedomax® "Type H" controllers and "Series 60" Proportional-Control Units—have been announced. Both are mounted in the Speedomax case when the equipment is to be used for proportional control. The Control Unit is also made as a separate instrument for use with the company's Speedomax Type G and Micromax® controllers. Both lines are among the equipment shown by L&N at the Metal Show, Chicago, Nov. 1–5, 1954. Folder sent on request. Leeds & Northrup Co. N-136

FISHER REAGENT MERCURY. The newest Fisher Reagent Mercury is available in a contamination-free polyethylene bottle which can be squeezed to yield a tiny stream from a dispensing tip or tapped for a single drop. The mercury is prepared with a process that selectively oxidizes and removes base metals, and, in addition, filters out oil and moisture. Analysts will welcome the new reagent for calibrating volumetric ware in the laboratory, and for a variety of reagent uses, including that of reducing agent in the analysis of iron, vanadium, copper, titanium, tungsten, and molybdenum; studies in the catalysis of sucrose inversion, etc. Fisher Scientific Co. N-137

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.

PANEL-MOUNTED *p*H INDICATOR. A new panel-mounted indicator for continuous measurement of *p*H or redox in manufacturing process is offered. The instrument is moisture-proof and gives accurate readings after less than a 1-minute warm-up, without the use of desiccants. It is also reported that the indicator is unaffected by line voltage surges, electrical pick-up, and zero drift. The a-c operated instrument can be used as a continuous indicator, with or without extra meter assemblies to duplicate readings. The indicator can also feed readings to a remote Speedomax® recorder. Leeds & Northrup Co. N-138

SELENIUM RECTIFIER. A new, low-cost bench selenium rectifier, with continuously variable output control ranging from zero to full rated power, has been announced. Designated Model 1020 F, the full wave design unit operates on an input of 110–120 volts, single phase, 60 cycle A.C.; with a rated output of 20 amperes 0–10 volts, D.C. An inductive capacitive filter provides an output with less than 5% ripple. Designed for extra heavy duty, continuous (24-hour) operation is possible; and provision is made for 20% overload for 2-hour periods. Furnished complete with 2% F.S. accuracy volt and ammeter, pilot light, starting switch, and fuse overload controls. Rapid Electric Co. N-139

EXTENDER PLASTICIZER FOR VINYL CHLORIDE. Excellent viscosity stability is imparted to dioctyl phthalate plasticized plastisols by HB-20, Monsanto Chemical Company's low-cost extender plasticizer for vinyl chloride, according to tests just concluded. HB-20, a partially hydrogenated alkyl-aryl hydrocarbon, is also recommended for vinyl insulated wiring for lampcords, Christmas tree lightcords, and other extrusions. Combined with Santicizer 160 as the primary plasticizer, and other low-cost extenders, it gives a practical and easily dry-blended formulation with good processing and electrical characteristics. It is an almost colorless, oily liquid. Because of its poor light stability, it is recommended for use only in dark-colored products. Technical bulletin available on request. Monsanto Chemical Co. N-140

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EMPLOYMENT SITUATIONS

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

Position Available

CHEMICAL ENGINEER, CHEMIST, OR METALLURGIST wanted by well-known metal producer. Must have thorough knowledge of electrochemistry for development work on electrodeposition and corrosion protection by means of metallic coating systems. Work involves some travel and liaison with cooperating laboratories and plants. Applicant must be energetic, cooperative, and have sound technical ability. Should have practical experience in plating. Submit complete résumé of education and experience to *Box A-258*.

Position Wanted

CHEMIST, 36, experienced in batteries, electroplating, general physical and chemical commercial testing, seeks South Jersey position. *Reply to Box 356.*

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Auto City Plating Company Foundation, Detroit, Mich.
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Buffalo Electro-Chemical Company. Buffalo, N. Y.
Burgess Battery Company, Freeport, Ill. (4 memberships)
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Gould-National Batteries, Inc., Depew, N. Y.
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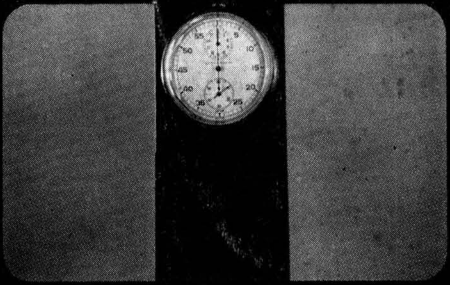
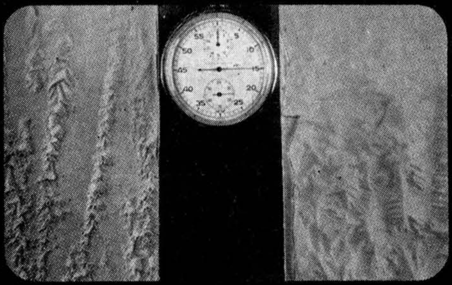
STRIPPING ENAMEL . . .

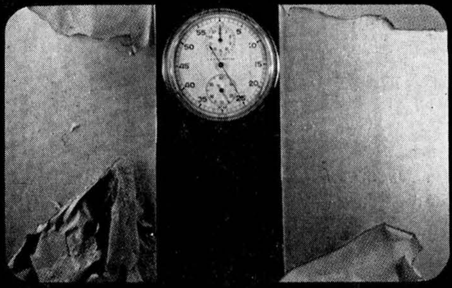
SAVING TIME



IMMERSED . . . THE WATCH STARTS!



15 SECONDS . . . WRINKLING TAKES PLACE!



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