

JOURNAL OF THE Electrochemical Society

Vol. 101, No. 11

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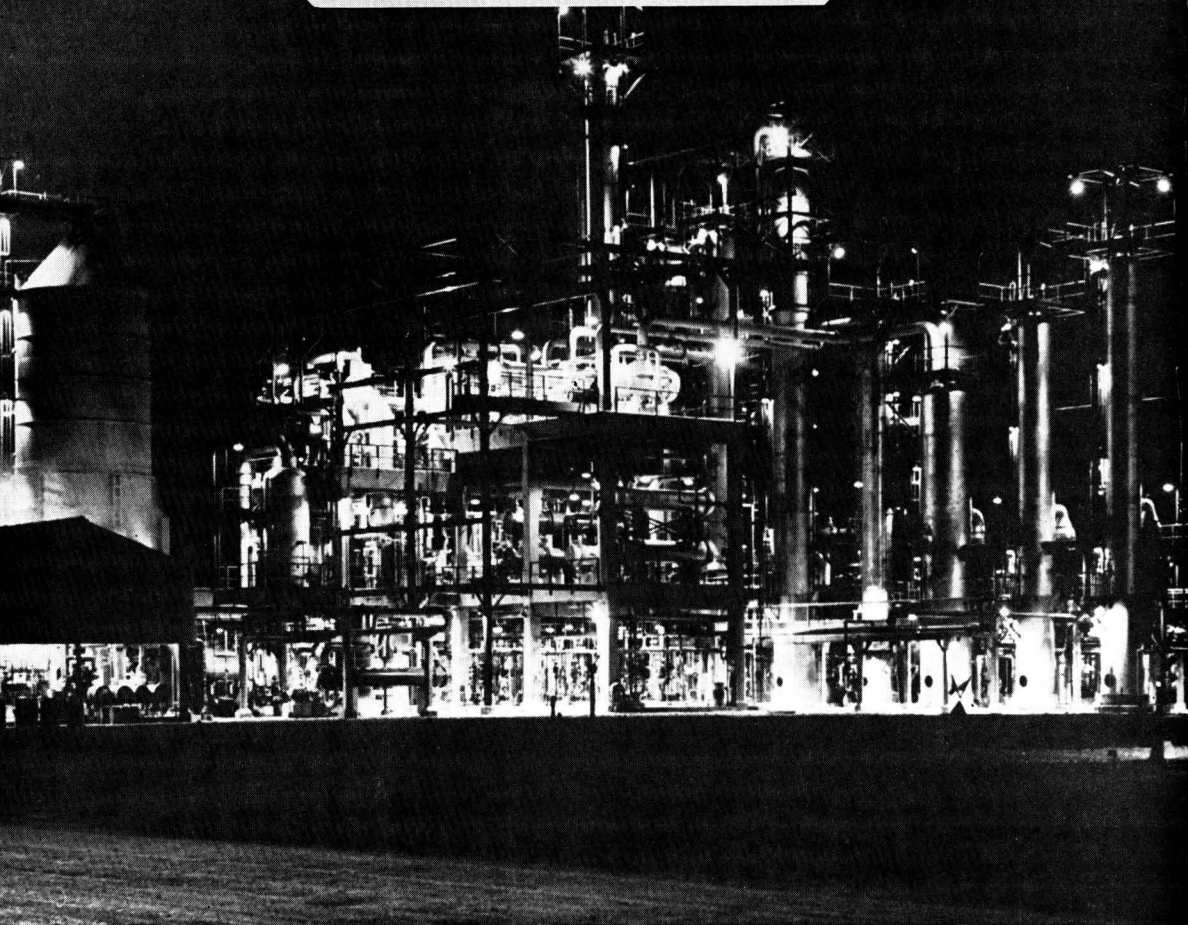
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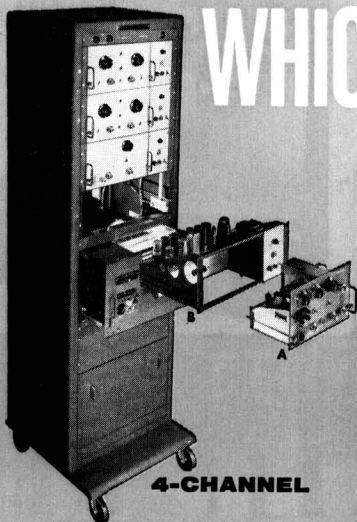


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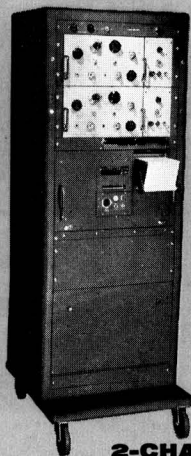
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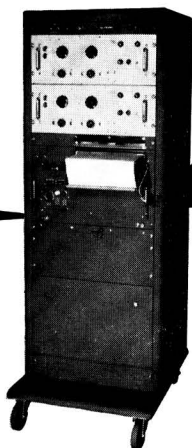
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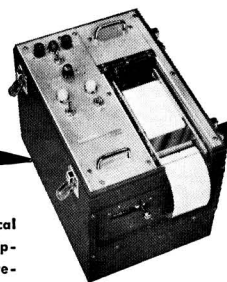


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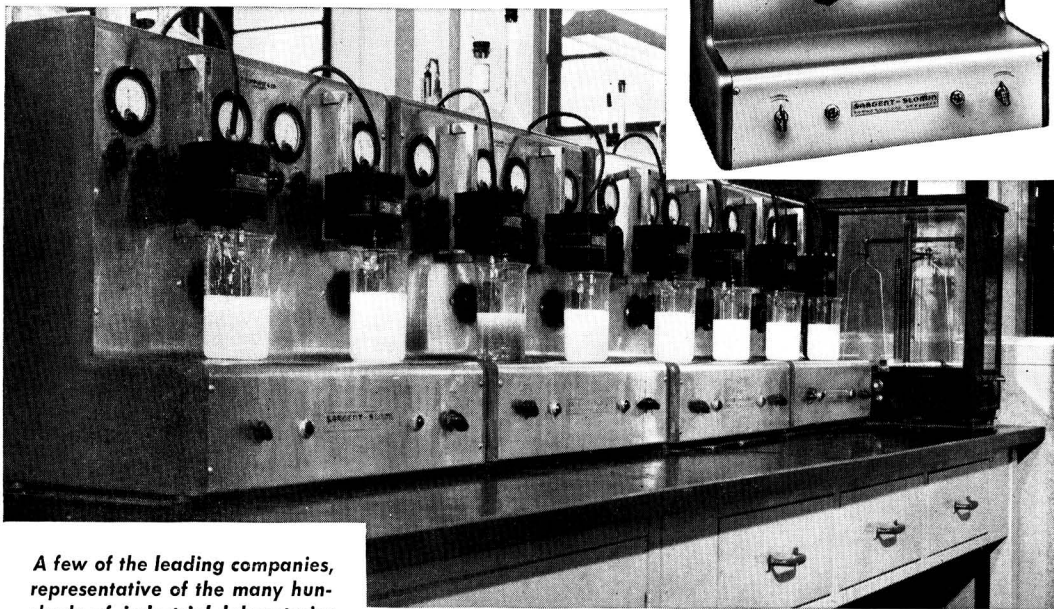
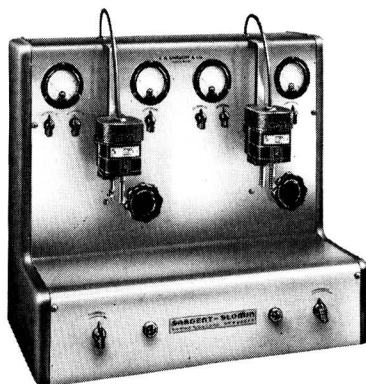
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The Crisis in Science Teaching

"IN PRODUCING scientists we need to run very much faster if we intend to win the race for survival" warns Professor Joel Hildebrand, one of America's great chemistry teachers and president-elect of the American Chemical Society. Discussing the fact that "western civilization with its fair degree of humanity, decency and freedom is menaced by a ruthless barbarism from the East," he concludes that "although we will not be saved from disaster by science alone, we will not be saved without science; all of it that we can muster!"

These words are most timely in view of the impressive evidence that the totalitarian nations are now producing substantially greater numbers of scientists and engineers than the free world. It is important that the country understand the seriousness of the situation and the necessity of training far larger numbers in the physical sciences and engineering. For not only must more young people be encouraged to enter these fields, but those who have chosen them must, if they are capable, be permitted to complete their education and then to practice their newly learned scientific or engineering professions. To draft such people for military service and give them nontechnical assignments is both stupid and hazardous from the standpoint of national defense. Yet it has been and is being done.

The alarming decrease in the number of graduates in the sciences is a direct consequence of the critical state of science teaching in the secondary schools. With a high school population that will increase 50% in the next six years, there is a growing decrease in both the number and the quality of science teachers. Compared with 1950, there were this year 34% fewer bachelor degrees conferred, but the decrease in the number prepared to teach science at the secondary school level was 56%. At present, 7000 new science teachers are needed annually, but only 5000 are graduated in science and less than half of these are actually going into teaching.

An inevitable result of this shortage of teachers is a decline in quality, particularly in the smaller high schools, for, when a teacher of the desired qualifications cannot be found, someone with lesser qualifications is hired. While it is to be expected that teachers who have majored in one science often will have to teach all science classes, a survey has shown that a considerable proportion of science teachers have had no science courses at all. It is very common to find that those teaching all of the high school science courses in a given school have had only one elementary course in science, usually chemistry or biology. Perhaps the most common arrangement of all is to ask teachers prepared in and teaching other subjects to teach in addition one class in science. Many schools offer chemistry and physics in alternate years. There is a growing practice of having the athletic coach teach chemistry and, realizing this, some colleges are including elementary chemistry as a requirement in their physical education curricula. The boys ought at least to make the football team!

There are two reasons for the present deplorable state of science teaching in the high schools. The first and foremost is the low salary level of the teaching profession. As Dean George R. Harrison says of secondary school teachers, "It does not take an eagle eye to see that they are more to be pitied than censured. While the national income has tripled, expenditures for public education have remained practically static. While factory wages have gone up an average of 56%, teachers' salaries have gone up an average of 7%." During this period, the chemical industry has grown more than fourfold and the electronics industry has increased ten times in size. It is no wonder that industrial opportunities have attracted a large proportion of the best

(Continued on next page)

Editorial (continued)

trained and most capable science teachers. Those dedicated individuals of first-rate ability who persist in teaching are finding it necessary to supplement their incomes by engaging in such outside activities as clerking in a store, driving a truck, and operating a shoe repair shop to cite only three instances recently observed.

Another and more insidious influence contributing to poor science teaching is the prevalent philosophy of the teacher's training schools that methodology is more important than knowledge of subject matter. Instead of receiving adequate instruction in science, students in these institutions learn, according to examples cited by Professor Hildebrand, "that education is the total procedure of reciprocating life responses by which personality, institutional progress and civilization are achieved. The business of education is to universalize the historico-scientific mindedness. . . . The spreading of this historico-scientific mindedness is the process of enriching the social soil," and finally that "society consists of persons plus psychosocial processes, plus the products of these processes, plus the patterns which result from them. And the whole system of relationships between these factors is what the sociologist calls culture."

The teacher-candidates who are fed this nonsense become science teachers and also public school administrators. As professional "educators," they have captured the state public school systems. The result is that all states require professional study in education for certification to teach but are less concerned about other subjects. For example, twenty-two states do not require any training in science for certification to teach science; others, however, do specify from 18 to 40 semester hours in the sciences.

It is coming to be recognized that the present declining trend in the selection of the sciences for careers will not be reversed until a marked improvement in both the number and quality of science teachers has been brought about. Only enthusiastic, inspired teachers who know their science and take pride in the profession of science teaching can influence young people in the choice of science as a career.

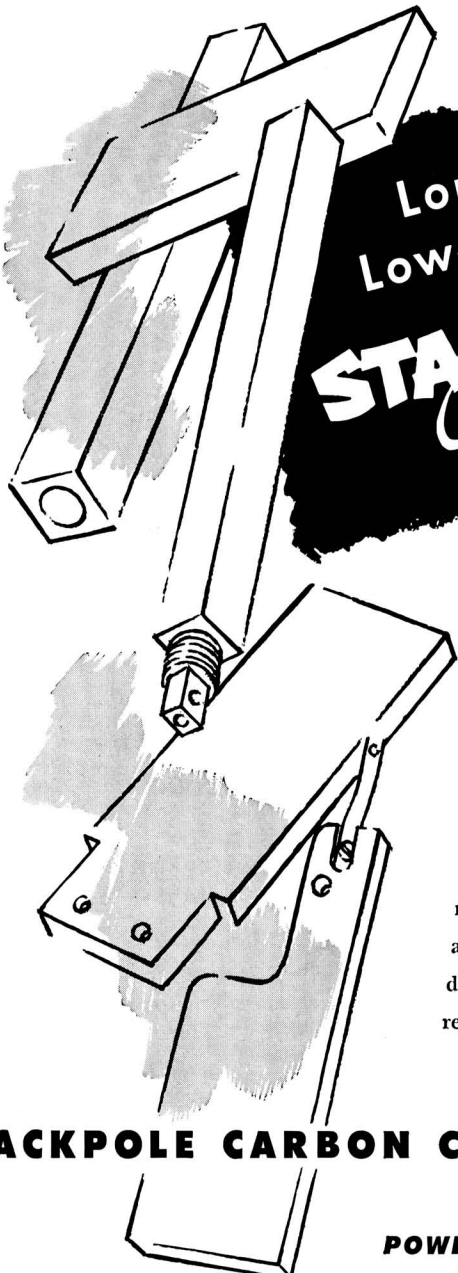
Solution of the problem of improving science teaching must lie in bringing about a marked increase in salaries and a change in emphasis in training, whereby knowledge of science as well as method of presentation will be required. Effort toward the attainment of these objectives must be undertaken primarily at the community level. Once the gravity of the situation is understood, thoughtful citizens will insist upon remedial action.

The scientific and engineering societies can play an important part through their regional groups and national organizations. For example, local sections of these societies should seek out the science teachers in the schools in their areas and encourage them to take part in technical and social meetings of their groups. Local sections of chemical societies should take the lead in persuading chemical companies to give summer employment to chemistry teachers, thereby enhancing both the income and professional experience of the teachers. Local sections should be willing to support science clubs and science fairs in the schools. They should create sentiment toward influencing local and state school authorities to reward and give special recognition to meritorious teachers. Activities of this sort will develop an atmosphere conducive to good teaching, as well as raise the prestige of the teacher.

The Virginia Academy of Sciences through its Junior Academy is doing a great deal to stimulate both student and teacher interest in science. Other state or regional scientific bodies might well sponsor similar junior affiliates and thereby promote wider participation and even competition in scientific programs.

Finally, the technical societies acting through their national organizations can be effective in influencing colleges, state educational authorities, and the public at large toward bringing about better science training for teachers. Professional societies and academies can do much to encourage science teachers by devising means to promote their professional standing.

—R. M. BURNS



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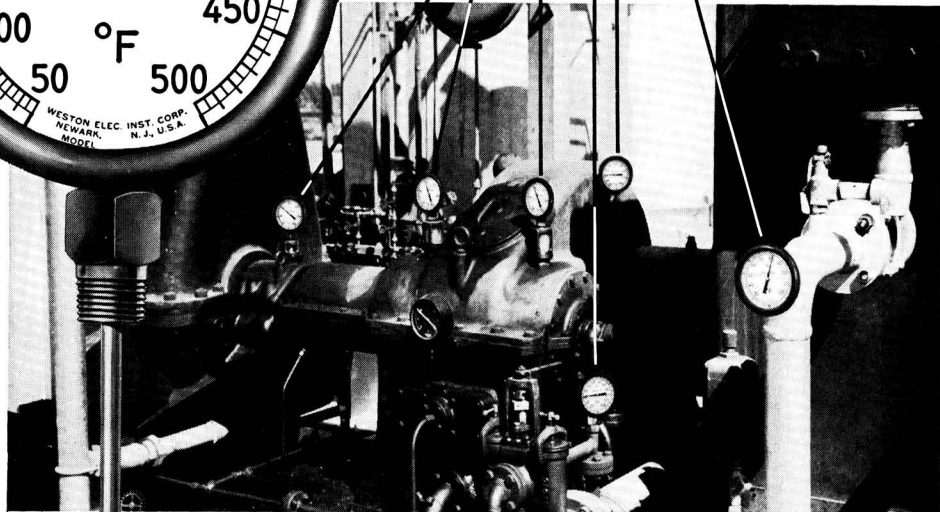
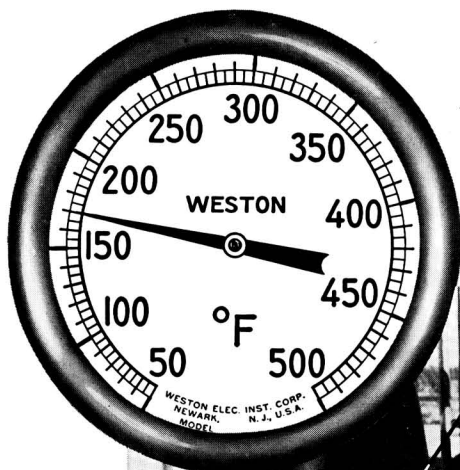
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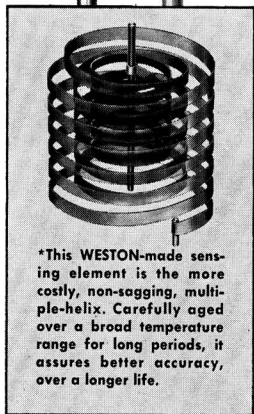
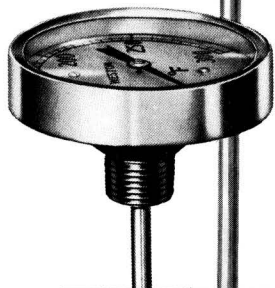
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Barium Sulfate as a Positive Plate Contaminant¹

J. F. DITTMANN AND H. R. HARNER

Eagle-Picher Company, Joplin, Missouri

Barium sulfate in fractional percentages is regularly used in the active material of negative plates in lead-acid storage batteries. At times, in preparing plates, some negative paste is accidentally mixed into positive paste, thus contaminating the positive paste with traces of barium sulfate. Rapid failure due to shedding has been traced to this barium sulfate contamination. Systematic tests show that as little as 0.0005% precipitated barium sulfate in positive paste markedly increases shedding on deep-cycling bench life tests. On the other hand, as much as 0.1% had no evident effect in overcharge bench tests, or in actual car service.

INTRODUCTION

The most widely used laboratory tests for storage battery durability, or life, involve successive cycles of fairly complete, or "deep", discharges followed by complete recharge. The test specified by the S.A.E. is of this type. It is widely used both as a laboratory tool for studying experimental batteries and as a procurement specification. In the latter case, batteries must yield at least a specified minimum number of cycles on the test to be considered acceptable.

Occasionally, a battery or group of batteries that should easily meet the test requirements fails prematurely due to excessive positive plate shedding. In many instances, the active material from the positive plates of these failing batteries has been subjected to spectrographic analysis. Usually, barium has been found as a contaminant in these positive plates. Since barium sulfate as precipitated *blanc fixe* is a usual constituent of paste for negative plates, finding barium in the positive active material is evidence of contamination of the positive paste with negative paste at some step in plate preparation. Since the same equipment is used alternately in many plants for manufacturing both positive and negative plates, it is surprising that such contamination is not more common.

In view of the fact that there is always this danger of contamination, it was considered most desirable to define more clearly the effect of barium sulfate as an impurity in positive paste, not only in deep cycling tests where the effect was first noted, but also in actual car service and in overcharge type tests.

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

EXPERIMENTAL

Nine lots of positive plates were prepared from nine carefully compounded batches of positive paste. The only known variable in the nine batches was the amount of barium sulfate as precipitated *blanc fixe* that was added, and which varied from none in the control mix to 0.10% as a maximum. The positive plates used 9% antimonial lead grids 1.72 mm thick. They were assembled into 15 plate elements with stock negative plates pasted in the same type grids. This assembly is rated at 85 amp-hr at the 20-hr rate and is intentionally deficient in positive active material. Forty-five batteries were prepared, nine for each of the three bench tests and eighteen for automobile service testing. In assembling the latter eighteen, positive plate groups from three different paste batches were assembled in each battery, i.e., formulas 1, 4, 7 in one battery, formulas 2, 5, 8 in the next, etc. By this means each positive formula was tested in six cars instead of only two, exposing it to a wider range of conditions of use.

Life Tests Used

S.A.E. cycling test.—This test (1) was developed shortly after 1930 and was later adopted as standard by the Society of Automotive Engineers. It is of the deep cycling type, subjecting the batteries to 4 cycles/day, each cycle comprising 40 amp-hr of discharge and 50 amp-hr of recharge with the batteries held at $110 \pm 5^\circ\text{F}$. Each week a capacity test determines battery condition.

Emark life test.—This test (2) was developed to simulate one type of automobile service—that of a taxi or delivery car. It is of the "shallow-cycling" type in that a discharge of 300 amp for 5 sec is given, followed by 6 min 30 sec of recharge at 10 amp, then a rest of 3 min 25 sec, after which the cycle is re-

TABLE I. Effect of barium sulfate in positive plates on battery performance under various conditions of test

BaSO ₄ content, %	0.0000	0.0005	0.001	0.003	0.005	0.0075	0.010	0.050	0.100	
<i>Battery Initial Capacity</i>										
Cycle	Rate	Temp								
1	5	80°F, amp hr	84	84	84	86	86	87	86	87
2	300	0°F, min	4.6	4.4	4.4	4.7	4.3	4.4	4.4	4.3
3	5	80°F, amp hr	85	85	85	87	87	89	87	87
<i>Battery Self-Discharge on 28 Day Stand at 80° F</i>										
Initial acid gravity	1.279	1.280	1.282	1.274	1.278	1.277	1.278	1.282	1.283	
Final acid gravity	1.241	1.237	1.237	1.239	1.238	1.237	1.240	1.242	1.242	
decrease	0.038	0.043	0.045	0.035	0.040	0.040	0.038	0.040	0.041	
<i>Life on "Deep-Cycling" S.A.E. Life Test</i>										
Yield cycle 32, amp hr	67	67	67	67	65	66	65	63	49	
Yield cycle 84, amp hr	67	64	64	57	56	54	50	42	25	
Yield cycle 188, amp hr	58	49	38	32	35	32	20	20	10	
Estimated life, cycles	250	210	175	150	145	140	110	90	50	
% Relative life	100	84	70	60	58	56	44	36	20	
% Pos. shed cycle 188	5	20	30	35	40	45	55	60	75	
<i>Life on "Shallow-Cycling" Emark Life Test</i>										
Yield cycle 860, amp hr	78	78	78	79	79	79	80	80	78	
Yield cycle 6951, amp hr	41	40	40	43	42	40	40	43	39	
Yield cycle 8468, amp hr	8	9	8	7	6	6	6	14	5	
Estimated life, cycles	6960	6950	6950	7000	6975	6950	6950	7000	6900	
% Pos. shed cycle 8468	Maximum estimated shedding 5%—No systematic differences.									
<i>Life on S.A.E. Overcharge Test</i>										
Yield after 1 week, min	8.0	8.2	8.2	7.5	8.4	8.3	8.5	8.1	8.0	
Yield after 3 weeks, min	3.9	3.3	3.2	4.1	3.3	3.5	3.2	3.1	2.8	
Yield after 4 weeks, min	0.65	0.40	0.60	0.70	0.30	0.25	0.40	0.25	0.45	
% Pos. shed, 5 weeks	Maximum estimated shedding 5%—No systematic differences.									
<i>Life in Automobile Starting and Lighting Service</i>										
Yield after 18 months, amp hr	65	74	52	65	75	40	64	75	42	
% Pos. shed, 18 months	6	5	14	7	5	14	8	5	13	

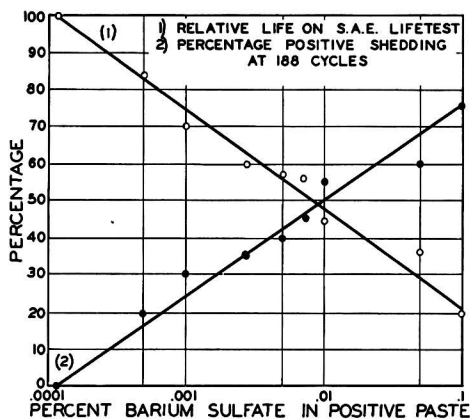


FIG. 1. Effect of barium sulfate content of positive plate active material on battery performance on S.A.E. life test.

peated. During the week the batteries are held in a water bath at $100 \pm 5^\circ\text{F}$. As in the cycling test, the capacity test is imposed once a week to determine battery condition.

Overcharge test.—This test (1) is to provide data as to the life of positive grids and of separators. Since these are major causes of failure in automobile use, this test is a useful one. The batteries on test are charged continuously for 110 hr at 9 amp, then allowed to stand for 48 hr on open circuit before receiving the weekly capacity test cycle. During the test, the batteries are held in a water-bath at $100 \pm 5^\circ\text{F}$.

Automobile service test.—Because of the great variation in the conditions of use, many thousands of batteries must be tested for definitive results. Except in a limited way it is, therefore, of little use for laboratory battery series. In the present case, many

possible auto test conditions were excluded by selecting the group of 18 test cars from among those owned by laboratory personnel. All were being used in the same kind of service and receiving similar mileage in the order of 10,000 miles/yr.

In addition to the above life tests, one set of the batteries was examined for self-discharge differences by being allowed to stand on open circuit for 28 days at 80°F.

Pertinent data have been summarized and are presented in Table I.

DISCUSSION

Barium sulfate had no detrimental effect on the initial capacity of the batteries. In fact, there is a trend to slightly higher 20-hr-rate yields with increasing barium sulfate content. Unless verified by additional testing, this cannot be considered significant since the variation is within possible experimental error.

There was no effect on self-discharge. The decrease in electrolyte specific gravity was of the same order for all cells and displays no trend.

No trend was shown on the Emark type life test, on the S.A.E. overcharge test, or in actual car service. Differences found in the batteries after car service were due to operating conditions of the car and not to formulation. The significant finding was that all batteries were still operative after 18 months in cars.

Quite a different story developed from the S.A.E. life test. The significant data are plotted in Fig. 1.

The life in cycles is an inverse function and the positive plate shedding a regular function of the logarithm of the percentage of barium sulfate in the positive plate active material.

From the above findings, the following conclusions may be drawn:

1. Barium sulfate contamination up to 0.1% of positive plate active material does not detract from the performance of batteries on noncycling tests or in average automobile use.

2. Barium sulfate contamination of positive plate active material is seriously detrimental to the life of batteries tested by a "deep-cycling" procedure and may be expected to be equally detrimental to the life of batteries used in "deep-cycling" service such as in battery propelled vehicles.

The only explanation for this harmful effect of barium sulfate is based on the theory that on "deep-cycling" the barium sulfate crystallites serve as nuclei for large lead sulfate crystals. Large lead sulfate crystals could then disrupt the bonding structure of the positive plate causing disintegration and shedding of active material.

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

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The Role of Inverse Segregation and Redistribution of Solute Atoms in the Freezing of Hypoeutectic Lead-Antimony Alloys¹

A. C. SIMON AND E. L. JONES

Naval Research Laboratory, Washington, D.C.

ABSTRACT

Inverse segregation has been found to occur in the lead-antimony alloys of the range of concentration used for battery grids. Because of the possible harmful effects of such large concentrations of antimony at the surface of the battery grid a study has been made as to the cause of this phenomenon. The extent of the antimony dispersion in the surface layer has been found to be larger than can be explained by any one of the existing theories of inverse segregation. The effect appears to be caused by an interdendritic flow of still molten alloy of near eutectic composition into the gap left between the semisolid crust and the mold face during the solidification contraction. The difficulty of inducing the nucleation of antimony produces a condition of supersaturation for the β phase in this layer while the lead continues to crystallize out at temperatures below the normal eutectic. The continually increasing concentration of antimony added to the decrease in temperature eventually brings a limit to supersaturation, whether or not nucleation is promoted by the mold face. The antimony present in excess of the eutectic concentration then forms primary dendritic crystals which grow until the eutectic composition is again reached, at which point eutectic crystallization occurs. The result is a surface film of antimony far in excess of the distribution found within the ingot.

INTRODUCTION

When a hypoeutectic lead-antimony alloy casting is examined a great deal more antimony is found in the surface layer than would be expected from the alloy composition. As the composition of the alloy approaches that of the eutectic the surface layer becomes almost entirely antimony instead of the expected eutectic. This effect is a factor of importance in the casting process and in the subsequent use of the alloy material. In the use of lead-antimony as a battery grid material this unequal distribution of antimony at and near the surface may be a factor in the adherence of the active material, as well as an influence on the rates of corrosion and growth. The presence of large amounts of antimony in the surface layer definitely influences the structure of the initial corrosion product that is formed and contributes to the deposition of antimony at the negative plate.

The present paper deals only with the investigation of inverse segregation itself. The effect of inverse segregation on battery grid performance will be reported at a later date.

The phenomenon of inverse segregation (decreased concentration of the solute constituent toward the center of the casting, with abnormally high concentration at, or near, the surface) is well known and has been reported in many alloy systems. Excellent reviews (1-3) include most of the literature on this subject prior to 1950. These analyze the existing

theories of inverse segregation in a critical manner and contain excellent bibliographies of prior papers on inverse segregation.

Two forms of inverse segregation have been reported: (a) a gradual decrease in the low melting point constituent toward the center of the casting, detectable only by chemical analysis; and (b) exudations at the surface of high concentration of eutectoid, rich in the low melting point constituent, which may or may not be accompanied by a gradual internal change of composition. The inverse segregation observed in the lead-antimony alloys conforms to type (b), except that the surface is covered with primary crystals of antimony rather than an antimony-rich eutectic.

None of the theories of inverse segregation adequately explain the extent of antimony segregation found at the surface of the lead-antimony alloy castings nor do any of them explain the primary crystallization of the β phase in the surface layer. Further investigation of this phenomenon therefore seemed advisable.

EXPERIMENTAL PROCEDURE

Both chill and slowly cooled castings were prepared from a series of lead-antimony alloys containing 1, 3, 5, 7, 9, 11, and 13% antimony, respectively. A microscopic examination was made of the surfaces and cross sections of the ingots. Since inverse segregation appeared principally as a surface exudation of the antimony-rich material there was little of value obtained from cross-sectional examina-

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

tion and the principal reliance was laid upon surface examination. Surfaces were examined in the as-cast condition; the castings were then etched with acetic acid-hydrogen peroxide solution (2 ml of 30% Superoxol to 48 ml of glacial acetic acid) and again inspected. This etch dissolves the lead and the lead-rich solid solution but does not appreciably attack antimony or the β phase. The antimony present in solid solution is precipitated as a very finely divided black soot-like film only upon the surface of the lead against which larger particles of antimony stand out brilliantly. There is, therefore, no difficulty experienced in differentiating between lead and antimony in the surface layer. The black film which obscures the surface of the lead-rich areas can be readily rubbed off, although it cannot be removed by washing. Rubbing, however, distorts the surface structure of the soft lead matrix. Scotch tape applied to this surface and gently pressed (but not rubbed) into contact with the surface by means of a very soft pencil eraser or other soft rubber pad was found to be very effective in removing this black deposit. If the etch is prolonged slightly, the thin surface layer of antimony is undermined and can be transferred intact to the Scotch tape. Thus, both sides of the antimony film can be examined as well as the new surface of the ingot revealed by the removal of the antimony. In one case this stripped film was subjected to x-ray analysis and identified as antimony as a check on other observations. Repeated etching and stripping in this manner revealed the structure to a considerable depth below the original surface.

On another series of castings, heavily plated with copper, taper sectioning (4) was employed to observe the structure of the very thin surface layer. Taper sectioning caused an apparent increase in the sectional thickness of the surface layers while the copper preserved the original surface contours.

Still another series of castings were made in a special mold, the two opposite sides and bottom of which were composed of aluminum while the other two sides were of transite. The top was left open to the air. Such a mold design insured very rapid chill casting at the cold aluminum faces and a progressive growth of the dendrites into the much more slowly cooled interior and provided a means of studying the effects of unequal freezing. All castings were approximately $1\frac{1}{4}$ in. high, 1 in. wide, and $\frac{1}{2}$ in. thick.

OBSERVED SURFACE STRUCTURE

Examination revealed that antimony appeared at the surface in excessive amounts under all the conditions that were investigated. The excess antimony that appeared on the surface increased as the antimony concentration in the alloy increased but to a greater proportional extent. Thus, an alloy that had

contained 10% antimony in the liquid state showed a surface after freezing that appeared to be almost entirely antimony.

For equal amounts of antimony, the alloys chill cast very suddenly showed the least amount of exudation of antimony on the surface and the surface structure agreed with the internal structure. Alloys cooled very slowly (less than $1^\circ\text{C}/\text{min}$) appeared to show no exudations but closer inspection revealed a high concentration of antimony at the bottom of the ingot (which was also the last portion to cool). The dendritic structure of the ingot was clearly revealed elsewhere on the surface by a withdrawal of the low freezing constituent, but at the bottom surface and a short distance up the sides the surface was smooth as if all the low freezing constituent had drained to this area. Alloys that were cast in a mold with unequal cooling of the mold faces gave the greatest evidence of exudations at the surface. Here also the greatest amount of exudation appeared at the more slowly cooled face and the surface structure was quite different from that found in the interior of the ingot.

For the alloys of low antimony content the surface antimony was concentrated at interdendritic and grain boundaries in a continuous layer that had no similarity to eutectic crystallization (Fig. 1).

As the amount of antimony in the alloy was increased the antimony-rich layer was found to cover the whole surface. This film, apparently continuous

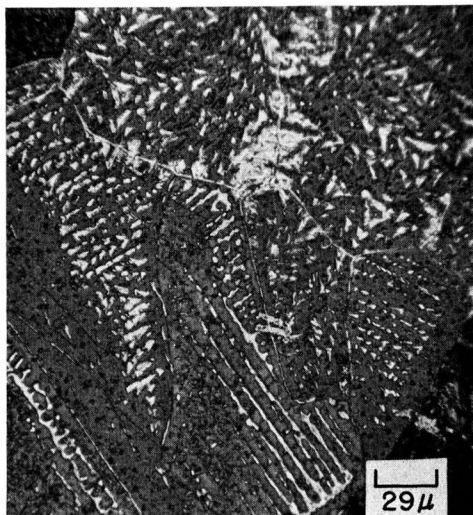


FIG. 1. Appearance of the vertical surface of chill cast lead-antimony ingot containing 2% antimony after an etch with acetic acid-hydrogen peroxide solution. Inverse segregation is indicated by excessive antimony (lightest areas) at interdendritic and intergranular extrusions. $300\times$.



FIG. 2. Appearance at vertical surface of chill cast lead-antimony ingot after etch with acetic acid-hydrogen peroxide solution. Antimony (light areas) covers almost the entire surface and shows primary crystallization although representing only 5% of the total alloy. 500X.

before etching, was found after etching to present a dendritic structure in which the antimony appeared as the primary crystallization and in amounts far in excess of the lead (Fig. 2). When this surface film was removed, a second layer was revealed which had the appearance of a true eutectic crystallization and in which the proportions of lead and antimony appeared to be normal. Beneath this second layer the true dendritic structure of the alloy was found.

For castings in which unequal cooling had occurred the still molten metal from the warmer regions was found to have flowed into the space between the frozen crust and the chill wall of the colder portion, forming a second antimony-rich film on top of that which had been formed by flow through the interdendritic channels (Fig. 3). The path of this flow was often plainly marked by the difference in crystal appearance and the fact that the frozen wave was actually visible, arrested by the freezing process before completely covering the original surface (Fig. 4).

Where the surface layer was thick, as in the case where flow had occurred from one area to another along the mold face, the surface was characteristically covered with tetrahedral crystals originating in the primary crystallization of antimony. Examination showed that while these crystals showed primary dendritic crystallization of antimony and a surface layer that was essentially antimony there appeared beneath the surface a layer of eutectic crystallization



FIG. 3. Surface area from vertical wall of unequally cooled lead-antimony ingot containing 2% antimony. Original surface containing a few interdendritic and intergranular extrusions of antimony has been overrun by a molten stream of antimony-rich material originating at a mold face of lesser chill. Last formed film can be distinguished by its disregard for grain boundaries and other crystal structure. (Acetic acid-hydrogen peroxide etch.) 300X.

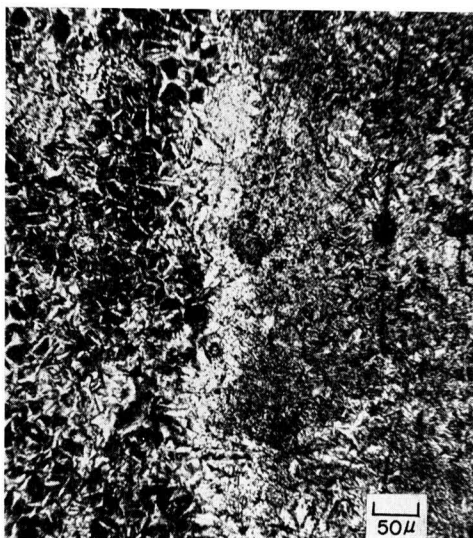


FIG. 4. Surface area from unequally cooled lead-antimony ingot containing 4% antimony showing crest of secondary wave of antimony-rich alloy (left) frozen in the process of covering the original surface film (right) of antimony-rich alloy. (Unetched specimen.) 150X.

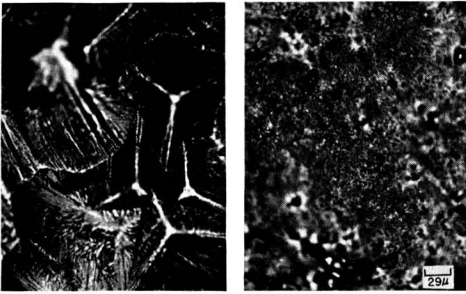


Fig. 5. Surface appearance of chill cast lead-antimony alloy with 9% antimony. (a) Before etching; (b) after etching with acetic acid-hydrogen peroxide solution and subsequent stripping of the surface film of antimony with Scotch tape. The subsurface layer here shown consists of an eutectic mixture of lead and antimony. 150X.

which nevertheless conformed to the general shape of the crystal (Fig. 5).

Taper sectioning confirmed the observations made at the ingot surface. A columnar dendritic growth was revealed a short distance inward from the ingot surface, separated from the surface by a layer of eutectic structure, while at the surface there appeared a very thin layer of antimony.

The appearance of the surface as viewed under the microscope left no doubt that the original frozen surface had withdrawn from the mold face through shrinkage of the ingot surface layer, expansion of the mold, or both. This space then appeared to have been filled by still molten material that flowed to the surface through interdendritic channels or flowed along the mold wall from regions still molten. The surprising feature is that the liquid metal flowing to the surface did not appear to have frozen instantly. Equally surprising is the fact that, when freezing did begin, primary crystallization of antimony should first occur, and to such an extent.

DISCUSSION

The type of inverse segregation that causes exudations of a low-melting point constituent at the surface is common in binary tin bronzes, phosphorus-tin bronzes, zinc-tin bronzes, leaded bronzes, leaded gun metals, and aluminum-copper alloys. For all of these alloys there are certain factors in common from which the following significant observations have been made (1, 3).

(A) Inverse segregation occurs only in alloys with a considerable freezing range.

(B) The exudation type of segregation is observed with alloys in which there separates a low-melting point constituent during solidification.

(C) Inverse segregation occurs only in alloys that contract during solidification.

(D) The presence of gas absorption tends to increase the effect.

(E) Inverse segregation increases with increasing rate of solidification with the exception that very rapidly chilled thin sections fail to exhibit this effect.

(F) Inverse segregation is favored by the formation of coarse columnar grains.

On the basis of these observations a comparatively simple explanation of inverse segregation is possible.

Redistribution of Solute Atoms during Freezing

At the instant a melt is poured into a mold at lower temperature there is formed a surface of intense supercooling and heat begins to flow from the interior of the liquid, through the interface, and into the mold. Immediately after contact is made, the region of supercooling or chill is confined to a very thin section of the melt, parallel to the chill wall, and the balance of the melt is essentially without a thermal gradient (5). After a brief interval a thermal gradient is set up that extends into the interior. When a thermal gradient is established, dendritic growth will proceed simultaneously from a great many points along the dendritic arms that first developed in the undercooled layer (Fig. 6). This secondary dendritic growth will extend along the thermal gradient toward the interior of the melt and the growth rate will depend upon the steepness of the thermal gradient. The steepness of the thermal gradient depends upon the thermal properties of the mold wall, the liquidus to solidus range of the alloy, conductivity of the solidifying metal, and the temperature level of solidification (6).

This growth produces a series of parallel dendritic arms extending from the surface layer well into the interior of the ingot. The spacing of these parallel dendritic arms has been shown (7) to increase with increasing concentration of the solute atoms and with deceleration of growth, and also to vary in the same manner as the ratio of the heat of fusion to the thermal diffusivity. These interrelating factors indicate that each growing dendritic arm of the crystal is surrounded by thermal and concentration gradi-

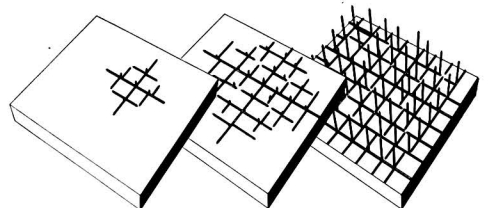


Fig. 6. Dendritic growth from mold wall into interior of melt. (a) Initial nucleation in the supercooled layer of melt next to the mold wall; (b) rapid dendritic growth parallel to mold wall to remove initial condition of supercooling in this layer; (c) dendritic growth toward the interior of the melt following the establishment of a temperature gradient.

ents that extend for considerable distances into the surrounding melt.

For the purpose of illustration the space occupied by the growing crystal may be considered as made up of an assemblage of cells (parallelograms) of practically uniform size with a growing dendritic arm occupying the longitudinal axis of each. Dimensions of the cells (spacing of the dendritic arms) are determined by the concentration and thermal gradients set up at the time that the dendritic arms were embryonic. Subsequent radial growth of each dendritic arm is restricted to the confines of the original cell because of the presence of surrounding cells. Conditions existing at successive stages of growth are therefore not exactly as depicted in Fig. 6 because the dendritic arms would not have a uniform thickness throughout their length, as shown, but would also grow in diameter as solidification proceeds.

Normally, in the case of diffusion to an expanding surface, the area of the diffusion field would increase continuously, but under the conditions outlined above the area of the diffusion field cannot increase. The concentration gradient will change continuously, however, affected by the concentration changes at the boundaries of the other cells.

The extent of dendritic growth for any instant can be calculated, if it is assumed that equilibrium conditions exist, by reference to the equilibrium phase diagram and application of the lever rule. The calculation can also be made for nonequilibrium conditions, if the assumption is made that diffusion into the solid is negligible while diffusion throughout the liquid is complete (8). Conditions applying for equilibrium and extreme nonequilibrium can then be compared graphically. All actual freezing conditions will occur somewhere between these extremes.

How this would affect dendritic growth is shown graphically in Fig. 7 for an alloy of 1% antimony in lead. The figure represents three stages in the growth

of two dendritic arms, parallel to a thermal gradient, as the temperature of point x varies from 320.5° to 250.5°C (608.9° to 482.9°F). As the temperature of point x drops there will be a progressive solidification of the remaining liquid portion upon the dendritic arm that includes point x , and the latter will progressively become thicker. At the same time there will be a progressive increase in the antimony concentration of the still liquid portion surrounding point x . The numbers in brackets indicate the percentage solidification at the indicated temperatures, while the unbracketed numbers represent the concentration of the melt at the solid-liquid interface. The dendritic arms are assumed to have equal growth rates and to be surrounded by others with similar conditions of growth.

For equilibrium conditions (solid line), with a temperature gradient as shown, the advancing boundary of solidification would assume in cross section the form indicated by the line ABCDE, and the boundaries AL and ER would be in contact with neighboring dendritic arms. The entire solidification of the dendritic arms would take place in the temperature interval between 320.5° and 314°C (608.9° and 597.2°F), with the composition of the melt at the beginning being 1% and increasing to 2% just prior to final solidification. The composition of the solid would approach 1.0% as a limit and at the moment of final solidification would have a uniform composition of 1.0%. At 314°C (597.2°F) there would be no gap remaining between the dendritic arms.

The boundary condition between solid and liquid metal for conditions of extreme nonequilibrium (broken line) are represented by the line LMBOP-DQR. Solidification in this case begins at the same temperature but extends over a much larger interval, reaching the eutectic temperature of 252°C (485.6°F). The melt also varies in composition along the interface, approaching the eutectic composition of 11.2% antimony just prior to final solidification. With a considerable gap still remaining between

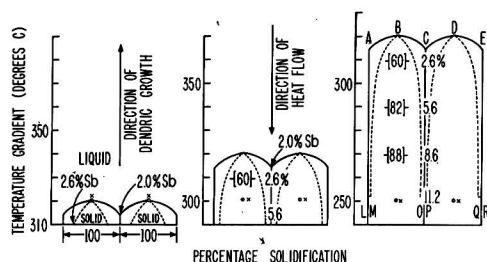


FIG. 7. Graphic representation of growth of parallel dendritic arms toward the interior of a melt under the influence of a temperature gradient. — Solidification under equilibrium conditions; - - - solidification under nonequilibrium conditions; [] percentage solidified at given temperature.

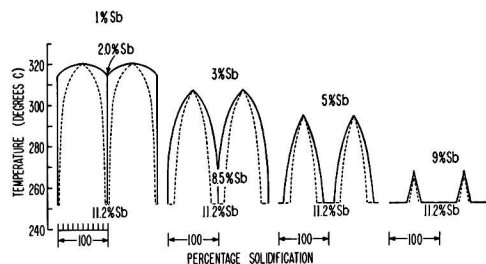


FIG. 8. Graphic representation of change in interdendritic channels for increase in antimony concentration. — Solidification under equilibrium conditions; - - - solidification under nonequilibrium conditions.

the dendritic arms even at the eutectic temperature, there is a definite possibility of interdendritic flow through the porous surface crust.

The space remaining between solidifying dendritic arms at the eutectic temperature increases as the amount of antimony in the alloy is increased (Fig. 8). This is true not only because of the decreased solidification taking place but also because the spacing increases with increasing concentration of the solute atoms (7). The length of the dendritic arms as compared with their thickness is dependent upon the steepness of the temperature gradient so that in chill casting quite long dendrites are possible before the surface layer is completely frozen. Fig. 7 and 8 are two-dimensional graphic representations of a three-dimensional effect. For any actual cross section the total solidification would therefore appear greater and the liquid layer surrounding each dendrite would actually appear thinner than represented here.

The assumption that diffusion in the liquid layer is complete, used here in the calculation of non-equilibrium conditions and previously by others (9-12), has been attacked (13) on the grounds that a diffusion coefficient of 1-10 cm²/day for liquid metals (14, 15) would be entirely inadequate to insure uniform composition of the melt during freezing. That the entire melt is not of a uniform composition is undoubtedly true, as witness the concentration gradient that exists between the tip and base of a growing dendritic arm. If the diffusion coefficient was sufficiently high, there would be diffusion from regions of higher concentration to lower with uniform solidification and elimination of dendritic growth. For actual dendritic growth, however, where the mass of liquid metal is, figuratively speaking, divided into many small cells in which diffusion distances are small, the assumption can be made without serious error that complete diffusion has occurred in the liquid cross section under consideration. Spacing between dendritic arms has been measured to be about 0.001 mm for cubic metals (7) and a large portion of this space is filled with solidified metal in the first part of the freezing interval when there is but slight change in the liquid concentration. In the final part of the freezing interval when concentration gradients are large, the diffusion would be operating through such short distances that the diffusion coefficient of 1 to 10 cm²/day would seem adequate.

However, if the above rate of diffusion is not sufficient to produce uniform concentration in the remaining molten layer, the argument is not basically altered. The effect of an inadequate diffusion rate would be to pile up an excess of solute atoms at the solidifying interface. This, in turn, would result in a

lower percentage of solidification at a given temperature and result in a larger space between dendritic arms when the eutectic temperature was reached. The net effect would be to push nonequilibrium conditions to a greater extreme than discussed above and thus increase the possibility of interdendritic channels in the outer crust.

Interdendritic Flow

While the interdendritic flow theory now seems to be generally accepted, the exact reason for an outward flow of metal between the solidifying dendrites has been the subject of some dispute. It has been suggested (16) that, as solidification proceeds, dissolved gases become increasingly concentrated in the residual liquid until the saturation point is exceeded, whereupon the gas is liberated and forces the liquid metal along the interdendritic passages toward the ingot exterior. Exudation in an 11% tin bronze does not occur when melting is performed in an oxidizing atmosphere, but becomes very noticeable in a reducing atmosphere (17, 18). Inverse segregation is greatest under atmospheres of hydrogen, water vapor, hydrogen sulfide, or methane (19). Similar results have been found for aluminum alloys (20). This evidence suggests that dissolved hydrogen causes severe segregation.

However, gas is not the sole factor or even a necessary one as demonstrated by experiments which show that inverse segregation can occur in alloys melted in a vacuum (21-25).

Lead reportedly dissolves less than 0.1 ml of hydrogen per 100 g of lead when near the melting point of the liquid metal (26). For oxygen a solubility of 0.2 ml per 100 g of lead has been reported (27), with a marked decrease in solubility for increasing additions of antimony. This volume of gas, while small, nevertheless constitutes better than 1% of the alloy by volume so that its liberation in the later stages of freezing could have an appreciable effect. However, it has been shown (25) that inverse segregation occurs in lead-antimony even when vacuum cast. One alloying constituent has been experimentally substituted for another in the interdendritic channels of a semisolid metal (28) thus proving that interdendritic flow is possible when motivated by purely gravitational forces. In the present investigation no internal porosity was found. Such porosity would be expected if gas was the motivator of interdendritic flow to the surface. The behavior of very slowly cooled ingots in which the low melting constituent withdrew from between the primary lead dendrites at the side surfaces and concentrated at the bottom surface of the ingot indicated an interdendritic flow caused by hydro-

static pressure of the still molten metal and the simple effort of a liquid to seek the lowest level.

In the case of steels cast in chill molds an air gap has been found to form between the mold wall and the frozen crust of the alloy (5). Microscopic examination of the surface of the lead-antimony alloys indicates that a gap is formed in this case also. Whether the gap was formed due to shrinkage of the original dendritic crust or expansion of the mold was not determined. Both factors probably occur to some extent and reinforce each other. Existence of an actual air gap such as occurs in steel appears to be unlikely. Instead the gap is probably filled continuously as it is produced by an inflow of molten metal. Whether or not the supercooled conditions survive long enough to cause complete filling will depend upon the conditions at the mold surface.

From the foregoing discussion it may be seen that no special force is necessary to cause interdendritic flow of metal after a gap is formed. The melt remaining between the solidifying dendrites will be near the eutectic composition. As this metal is forced into the gap by the hydrostatic pressure of the liquid interior, that portion of the liquid moving toward the surface from more remote regions will be brought to the eutectic composition. The metal flowing to fill the gap would therefore be expected to have essentially eutectic composition, whatever the composition of the original hypoeutectic melt.

Primary Crystallization of Antimony

Presence of a surface layer of antimony-rich phase in which lead appears as only a minor constituent is surprising. From the foregoing discussion a eutectic composition would be expected at the surface, but the interdendritic flow theory is inadequate to explain a structure in which antimony is plainly far in excess of the eutectic amount. In addition, antimony shows unmistakable evidence of primary dendritic crystallization and has the same crystal structure as it exhibits in the hypereutectic alloys where primary crystallization of antimony is to be expected.

Primary crystallization of antimony could occur in either of two possible ways. Either primary crystallization of antimony has occurred at the mold surface at the moment of initial chill or antimony has formed primary crystals from the eutectoid solution that flows into the air gap subsequent to the initial freezing at the mold face.

Primary crystallization of antimony at the surface in the initial chill could only occur by some process of phase inversion whereby the antimony crystals were momentarily precipitated before the expected and usual crystallization of lead crystals. Such a condition might be brought about by the extreme condition of chill and resultant super-

cooling produced at the moment of first contact of molten metal with mold surface. This would imply a change in the liquid prior to solidification. Theories of this type have been advanced and were considered as a possible cause of the primary crystallization of antimony.

Re-examination of Smith's theory of mobile equilibrium (29), Benedick's theory of the Ludwig-Soret effect (30), Hanson's (31) and Johnson's (32) theory of undercooling, and Ubblohde's (33) theory of minimum volume change do not suggest any mechanism that would so completely invert the normal order of precipitation as to allow primary crystallization of antimony prior to the solidification of the α phase crystals. In addition, the above theories have been more or less discredited either because of lack of favorable evidence or actual conflict with observed phenomena. Recent demonstrations (34-36) that metals can undergo extensive supercooling in the absence of nucleating agents, however, suggest a possible mechanism of phase inversion. If the molten metal were to be heated to a temperature sufficient to destroy all nuclei for lead nucleation but insufficient to destroy those effective for antimony, then the liquidus curve for the hypereutectic alloys could conceivably be extended into the hypoeutectic region, provided the lead remained supercooled and did not precipitate. Primary crystallization of antimony could then occur in regions where lead would normally be expected to appear.

Careful investigation, however, leads to the conclusion that antimony crystals were formed subsequent to the formation of the metal crust of primary lead crystallization and not at the instant that the molten metal first contacted the mold face. This conclusion is based upon the following considerations.

(A) In alloys of low antimony concentration, primary crystals of antimony (surface film) did not completely cover the surface but were concentrated at grain boundaries and interdendritic boundaries. If initial precipitation of antimony (inverse chill) occurred at the mold face, the distribution of the primary crystals would be expected to be random. Concentration at grain and dendritic boundaries indicates prior formation of a primary lead dendritic structure.

(B) The greater the differential between mold temperature and alloy freezing point the less the amount of antimony film present at the surface. Extremely rapid chill produced practically no exudations in alloys with low concentration of antimony. This is the opposite effect to that expected from an initial freezing of antimony due to surface chill.

(C) In the ingots that were adjusted for conditions

of unequal cooling, the greatest exudation of antimony and the appearance of well-formed tetrahedral crystals of antimony occurred at the face of lesser chill which is likewise contrary to a concept of surface chill.

(D) In very slowly cooled ingots, exudations occurred as a result of drainage, and primary antimony crystals were present only at the bottom of the mold which was also the last surface to cool (mold heated from below). In such slowly cooled ingots (mold and melt both originally above the freezing point of the melt) surface chill should be absent and the presence of primary crystallization of antimony at the warmest point of the mold suggests the alternate mechanism.

(E) In those cases where visible flow of metal could be traced across the original surface, the number, size, and perfection of the antimony crystals was greater on the secondary surface than on the primary.

(F) If primary crystallization of antimony is due to supercooling of lead at the initial chill surface, then the presence of nuclei for the crystallization of lead should prevent this supercooling and lead should precipitate first, in the normal manner. The ability of solid metal or metal powder to promote homogeneous nucleation of its own melt has been demonstrated (37). Castings made in a lead mold, however, continued to show primary crystallization of antimony at the surface.

(G) It has been demonstrated (36) that the more complex type of crystal structures show a greater tendency to supercool and that antimony shows a greater tendency to supercool than lead. Considering also that at the moment of initial chill large masses of metal are involved, it does not seem likely that lead could be supercooled to any such extent that antimony would first precipitate. More logically, antimony could be expected to supercool in the solution of eutectic composition that is extruded at the surface. In such a solution most of the heterogeneous nucleating agents would have been filtered out by passage through the narrow channel between solidifying dendrites. The mass of metal would also be separated into small droplets, a necessary condition for extreme supercooling (36). Due to a difference in crystal structure and lattice spacing the lead could not act as a nucleating agent for the antimony (37). Primary crystallization of lead could continue upon existing lead surfaces until the antimony became sufficiently supercooled to precipitate or until the molten solution was brought into contact with the mold face where nucleating agents might be present.

The primary crystallization of antimony is therefore considered to take place as a consequence of interdendritic flow of a melt of practically eutectic



FIG. 9. A portion of the field of view to the left of the center of Fig. 4, considerably magnified. The tetrahedral shape of the individual crystals and the nature of the dendritic structure indicate oriented primary growth of antimony in the surface layer. 300X.

composition into the gap left by the cooling of the metal. Lack of nucleating agents produces supercooling of the antimony while the lead continues to precipitate with consequent enrichment of the remaining metal in antimony. The primary dendritic crystallization of antimony apparently occurs at the colder mold surface, and dendritic arms extend through the still liquid melt filling the gap to the original metal crust. The observed appearance of small tetrahedra in the new surface with the dendritic arms extending along the tetrahedra edges in the [100] directions (Fig. 9) agrees with the report that surface crystals of castings of rhombohedral metals usually have a preferred orientation with the [111] direction normal to the cold surface (38). Solidification of the antimony in the layer brings the remaining melt to the eutectic composition and eutectic crystallization occurs within the primary antimony dendritic structure. Continued solidification of the liquid eutectic causes a volume decrease and the metal recedes from the mold face and the sides of the tetrahedra so that they become exposed in relief at the surface.

SUMMARY AND CONCLUSIONS

Inspection of commercially cast lead-antimony battery grids revealed the same phenomenon of excessive antimony at the surface as was found in all laboratory experiments. Laboratory experiments show that the excess amount of antimony in the sur-

face layer increases with increasing antimony content of the alloy and decreases with increasing chill. The observation that exudations decrease with increasing chill does not appear to check with previous reports. However, the terms slow chill and fast chill are relative. Castings referred to herein were made in small molds, of which at least two sides were aluminum, while some of the previous work is based on very large ingots cast in sand molds. Exudations observed on the very slowly cooled ingots (in metal molds) although highly localized in one portion of the casting probably represented as great a degree of segregation as did the more uniformly distributed (and much more noticeable) exudations of the more rapidly cooled specimens. Unequal cooling at various mold faces appeared to be as important a factor on inverse segregation behavior as was rate of chill.

Whether considered to be beneficial or harmful, inverse segregation in the lead-antimony alloys is a factor of importance. For some applications, inverse segregation may have advantages. Improved brightness and tarnish resistance result from the presence of a surface layer of antimony, and the effect of the phenomenon is to seal off and prevent any surface appearance of shrinkage cavities (except on the last surface to cool, which acts as a feeder). Whether such a layer would contribute to the physical properties of the alloy is problematical. The antimony layer is very thin and would not be expected to contribute materially to hardness or wear resistance, but the layer of eutectic material beneath it may reach a considerable thickness. Interdendritic flow of still molten alloy into the cavity left by shrinkage of the original frozen crust makes possible close casting tolerances and undoubtedly is in part responsible for the onetime belief that lead-antimony alloys expanded during freezing.

Inverse segregation may prove detrimental in applications involving corrosion resistance, such as storage battery grids. Preferential leaching out of antimony from the surface of lead-antimony alloys when subjected to anodic corrosion in sulfuric acid has been previously reported (39). Such action will have a twofold effect: (A) the surface antimony and eutectic structure extend from the surface into the interior of the casting along the interdendritic channels so that a penetrating type of corrosion may occur; (B) if the battery paste is applied to the as-cast surface, subsequent forming will remove the thin antimony layer and the exposed antimony in the surface eutectic so that poor electrical conductance and poor adherence of the active material would seem likely. Since the resulting surface will be much rougher, however, the active material may tend to adhere more firmly. Which effect pre-

dominates remains to be determined from future investigation.

The effect of inverse segregation on casting should also be pointed out. As already stated, formation of a second surface film tends to cover over any defects in the original frozen surface so that sound, pore-free castings of close dimensional tolerance are possible when the temperatures at the various mold faces are properly regulated and a proper feeding head of molten metal is provided. If all mold faces are equally chilled, however, then internal porosity should result.

The phenomenon of inverse segregation appears to be intimately associated with dendritic growth. Factors that tend to prevent dendritic growth should also tend to eliminate inverse segregation. While there is a possibility that supercooling of the eutectic and primary crystallization of the antimony could be prevented by the use of proper nucleating agents incorporated in the mold facing (37) or in the melt, there would still be a layer of eutectic structure and composition formed at the surface.

In some cases where excess antimony at the surface may be detrimental, as possibly for battery grids, the simplest solution would appear to be the removal of the surface film by chemical or electrochemical means before subsequent operations are undertaken.

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

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Electroluminescence with Nonsinusoidal Fields¹

SOL NUDELMAN² AND FRANK MATOSSO

U. S. Naval Ordnance Laboratory, White Oak, Maryland

ABSTRACT

Electric fields in the form of square or rectangular waves, saw-tooth waves, and exponential waves were applied to an electroluminescent phosphor. The light output contained green and blue luminescence bands, which were examined separately by means of filters, a photomultiplier, and an oscilloscope. Square wave fields produce luminescence peaks whenever the field is changing, followed by a decline in luminescence when the field is steady. Peak heights increase proportionally to about the fourth power of the field strength. They decrease with increasing frequency for the green band, while for the blue band they first increase up to about 2000 cps and then decrease. The decay obeys power laws with different exponents before and after a critical time of about 0.7 msec. A rectangular field pulse of greater duration than the critical time produces, in the green band, peaks of equal total intensity at the field reversals; in the blue band, the same excitation produces peaks with equal changes in intensity. Other field shapes produce peaks of luminescence whose heights and shapes depend on field shape and duration of the steady field before it is changed. Additional peaks in the green band appear whenever the field begins to decrease.

Observations are interpreted by using the following assumptions: excitation is due to collision processes of accelerated electrons; green luminescence involves transitions to the conduction band and to traps; blue luminescence is caused by transitions within a luminescence center; the effective field changes in time because of the development of polarization charges. Additional peaks in the green band are due to recombination processes of the polarization charges.

INTRODUCTION

In general, experiments on electroluminescent phosphors have been conducted with d-c or sinusoidally varying electric fields. These investigations have already offered valuable information and have led to conjectures on the mechanisms involved in electroluminescence (1). Additional information on the fundamental processes can be expected from application of nonsinusoidal field changes, particularly in the form of square waves, since in these cases all effects related to duration of the field show up more clearly, and the influence of the field as such can be better separated from the influence of the manner of its application. Here, therefore, fields have been applied in the form of square pulses, saw-tooth waves, rectangular pulses variable in width and repetition rate, and exponential waves to an electroluminescent ZnS:Cu, Pb-phosphor.³ It was necessary to make the observations separately for the green and the blue luminescence bands (2) of this phos-

phor since characteristic differences in the electroluminescence properties of these two regions were found.

Quantitative measurements with respect to field dependence, frequency dependence, and decay laws were made on the electroluminescence patterns [brightness waves (3)] obtained by using square wave electric fields. For other field shapes only qualitative observations are reported.

Work related to this has recently been published on the influence of step functions on the time-average light output (4), on oscillograms obtained with trapezoidal waves (5) and other field shapes (6).

Although a complete and quantitative interpretation of every experimental detail is as yet impossible, sufficient information seems to be available to justify a discussion of some mechanisms contributing to electroluminescence in the light of the present observations. Other workers have suggested basic mechanisms that are relevant to some of the results of this study (1-3, 7-11). These proposals, either in their original or in a modified form, are incorporated with those given here in order to obtain an integrated picture.

EQUIPMENT AND PROCEDURE

The fields were produced by using generators giving a variety of signal wave shapes. The genera-

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² Also at the University of Maryland, College Park, Maryland.

³ Sylvania Electric Products Inc., Bayside, N. Y.

tors for square waves and saw-tooth waves were variable from 10 to 10,000 cps, while a pulse generator variable in pulse width and repetition rate had a range of 100–1000 cps. A direct coupled amplifier with a rise time under load of less than 10 μ sec supplied an output peak to peak voltage of 0–320 volts. Exponential wave shapes were obtained by feeding a square wave into a square wave amplifier with a large RC time constant in its output circuit. This unit had a rise time under load of 250 μ sec, which could be increased still more by appropriate condensers. It supplied a continuously variable peak to peak voltage of 0–4000 volts.

Light output from the phosphor was observed by a 1P21 photomultiplier tube followed by a direct coupled oscilloscope. In general, data were obtained by taking pictures of the signal trace on the oscilloscope, then reading these films with an optical comparator.

The electroluminescent phosphor investigated was in the form of a cell containing a ZnS:Cu, Pb-phosphor³ exhibiting predominantly green light at excitation (12). Different samples of these green cells gave essentially equal results. In order to separate observations for the blue and the green luminescence band of this phosphor, a Wratten filter No. 21, which transmits wave lengths above 5300 \AA , or No. 36, which transmits between 3700 and 4600 \AA , was used.

EXPERIMENTAL RESULTS

Square waves.—When a square pulse of about 10 μ sec rise time is applied to the electroluminescent phosphor, the light output exhibits sharply rising peaks at the time of every field change. The peaks are followed by decreasing light output or “decay”, which generally does not have time to reach zero light output before the appearance of the next peak. The resultant luminescence pattern contains, therefore, a varying component or “ripple” superimposed on a steady background. All measurements of luminescence intensity, as peak heights or decay curves, are taken from the level of zero light output (“reference level”), which corresponds to the oscilloscope trace obtained without field.

For the same potential difference, the luminescence pattern is generally the same, whether the field is reversed in direction or simply applied and then removed.

Fig. 1 is a reproduction of an oscillogram made with three exposures for different field strengths. Besides illustrating the general peak pattern obtained with square wave fields, this figure also shows that with increasing field it takes less time for the luminescence to reach the maximum of the peak.

Dependence of height of luminescence peaks on

the repetition rate of square pulses is shown in Fig. 2. As the frequency increases, green peaks decrease in height, while blue peaks increase to a maximum value, then decrease. Experiments with manually switched D. C. indicate, however, that green peaks also decrease at extremely low frequencies, i.e., below about 2 cps. Voltage at the cell was maintained constant for these measurements.

The frequency dependence of the peak heights can be described empirically by a formula like

$$I_p = A + B \log f$$

over the frequency range 10–10,000 cps for the green peaks, and up to about 2000 cps for the blue peaks. I_p is peak height, f , frequency; A and B are constants.

Dependence of the steady background on repetition rate is also shown in Fig. 2. These curves appear to have some of the characteristics of the curves shown by Waymouth (2), obtained for the time-average light output with sinusoidal fields. There, too, the green electroluminescence increases with frequency from zero to a steady maximum value in the vicinity of 1000 cps, while the blue intensity is still growing in a nearly linear manner at about 2000 cps; but, in addition, a decrease is found in the mag-

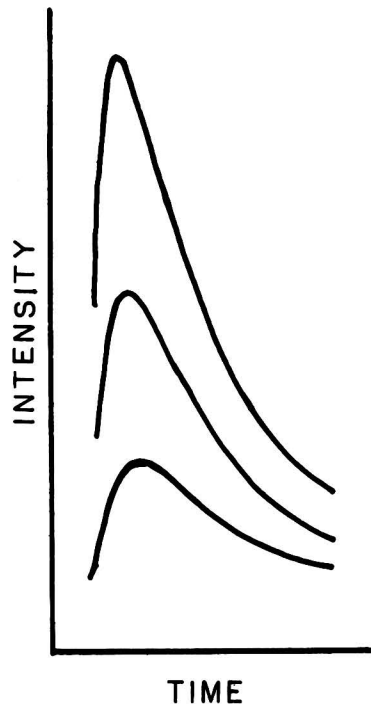


FIG. 1. Triply exposed oscillogram for blue electroluminescence, square wave fields, 90 cps, 250 μ sec rise time.

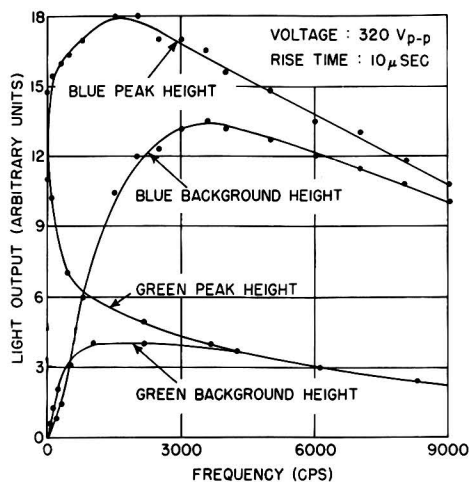


FIG. 2. Peak and steady background heights vs. repetition rate. Curves for green luminescence not drawn to same scale as for blue luminescence. Ordinates are measured from the reference ordinate for zero light output.

nitide of the steady background for both blue and green luminescence at sufficiently high frequencies. The analogy to Waymouth's results is understandable since the time-average light output is determined, to an appreciable extent, by the steady background.

Dependence of the height of the luminescence peaks on the field strength is shown in Fig. 3. Green and blue peaks grow with increasing field strength, although the green peaks do so at a more rapid rate. The curves of Fig. 3 may be described by power laws in the form $I_p = AE^n$, except for the low field region

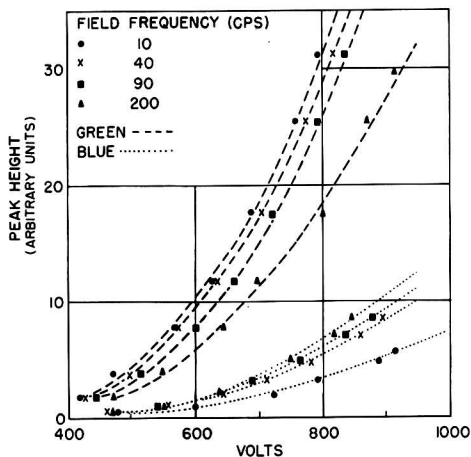


FIG. 3. Peak height vs. applied voltage. Curves for green luminescence not drawn to same scale as for blue luminescence.

of the curves for the blue peaks. The values of n obtained are 4.3 and 3.8 for the green and blue peak heights, respectively. It is also possible to represent the curves by a law of the form $I_p = aE^2 \exp(-b/E)$ as is found also by Destriau (3), with the exception that at frequencies higher than about 100 cps experimental curves of the blue luminescence depart from this relationship.

Fig. 4 shows decay curves in semi-log or log-log representation. Since the longest linear region appears in the log-log representation, it is preferable to describe the electroluminescent decay by power laws of the form $I = At^{-m}$. Furthermore, the early "linear" region of the semi-log plots is still more complex when observed with an enlarged time scale.

"Natural decay" was obtained after exposing the phosphor to weak radiation from an Argon lamp.

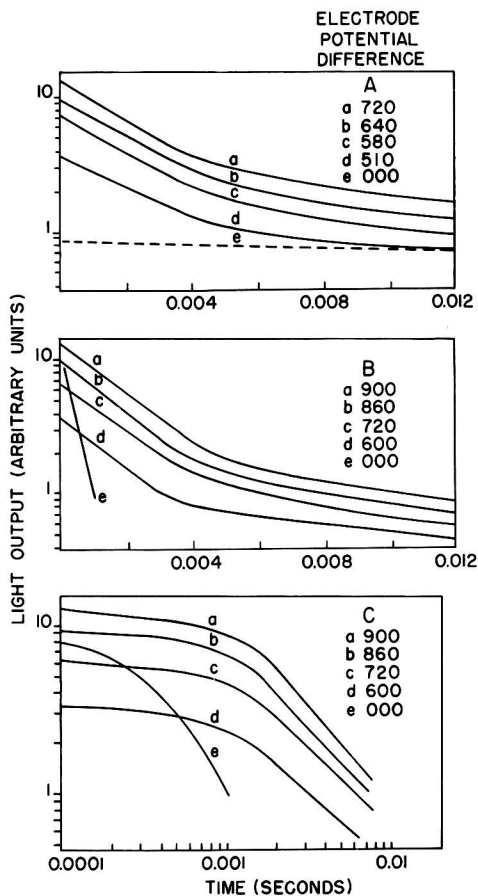


FIG. 4. Decay curves, 10 cps, 250 μ sec rise time. (A) Green luminescence, semi-log; (B) blue luminescence, semi-log; (C) blue luminescence, log-log.

The natural decay curve for the blue luminescence appears to be strictly exponential, while that for the green band is more complex. The blue natural decay is much faster than decay of the blue electroluminescence, while the natural decay curve for the green band declines at a slower rate than the corresponding electroluminescence decay.

Slopes of the decay curves vary somewhat with the field. This is particularly noticeable in Fig. 4c for the late decay of the blue band. However, for higher frequencies and for decay curves of the green luminescence in general, there is much less change, if any, of the slopes. There is also a variation of the slopes with frequency for constant field strength, particularly for the late decay of the blue luminescence where, for example, values of m vary from about 0.72 at 10 cps to 0.95 at 90 cps (at about 800 volts) (13). If the rise time of the field was changed, there was again a distinct change of m . Similar remarks would apply to the constants of an exponential decay law.

Rectangular pulses.—When fields of rectangular pulses like those indicated in Fig. 5 are applied to the phosphor, with different times t_1 and t_2 , observations reveal a marked qualitative difference between the green and the blue luminescence.

The significant features are: if t_1 is larger than about 0.7 msec, the blue electroluminescence peak increments, P_1 and P_2 in Fig. 5, are about equal, while for the green luminescence the heights H_1 and H_2 are of about the same magnitude. If t_1 is decreased to less than about 0.7 msec, the increment P_2 of the blue peaks becomes smaller. This critical time is of the same order of magnitude as the

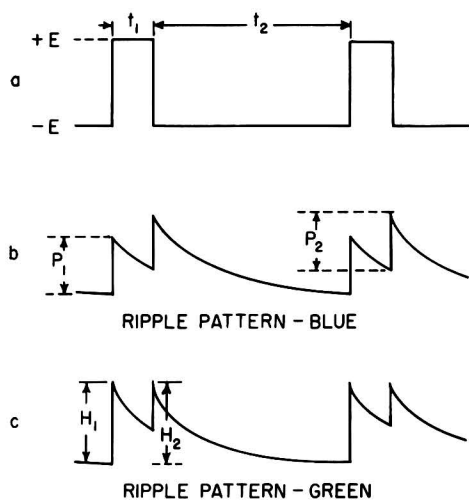


FIG. 5. Luminescence patterns for rectangular wave shapes.

transition time observed between the two linear decay regions in Fig. 4c.

Also, H_2 of the green luminescence begins to change its value if t_1 becomes smaller than the critical time. The complex quantitative details of the electroluminescence observed at small pulse time are the subject of a separate investigation and are not relevant to the discussions of this paper.

The patterns illustrated in Fig. 5 were produced by electric fields of 10 μ sec rise time. Fields with longer rise times give similar results although they are not as well defined.

Exponential and saw-tooth fields.—Fig. 6, 7, and 8 are examples of oscillograms taken with a dual beam d-c oscilloscope showing a variety of electric field wave shapes and corresponding electroluminescent patterns. These oscillograms have peaks labeled by different letters. General observations pertaining to these peaks are as follows.

The A and B peaks begin to grow whenever the applied field starts to grow from zero. The A peaks, observed at sudden field reversals, have the same appearance as peaks for square wave fields. D peaks are essentially identical with A peaks, except that they occur on sudden field removals.

The C and C' peaks appear when the applied field starts to change from some steady value. They exist in the green band only and are observable only on relatively slow field changes since, for rapid field changes, A peaks would hide the C peaks. C peaks

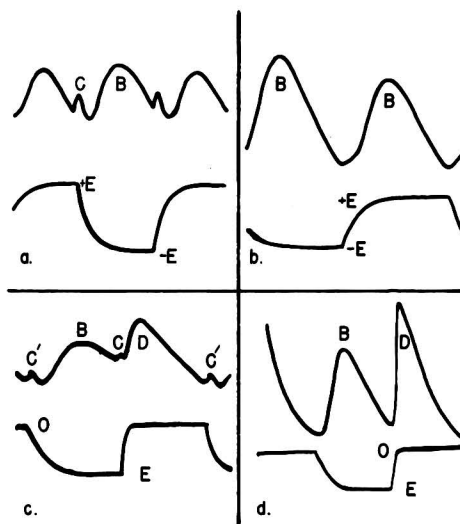


FIG. 6. Exponential fields, 500 cps, reversed and unidirectionally pulsed. (In the oscillograms in Fig. 6, 7, and 8, pictures a and c refer to green luminescence; b and d to blue luminescence. In each picture, the upper curve shows the ripple pattern; the lower curves, the corresponding applied fields.)

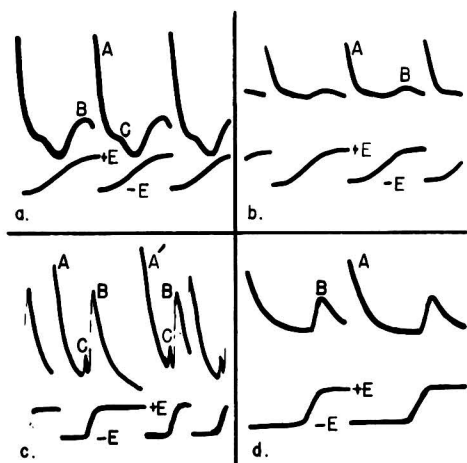


FIG. 7. Saw-tooth fields. (a) 100 cps; (b) 250 cps; (c) modified saw-tooth, rise time, 2.8 msec; (d) rise time, 2 msec.

occur when the field starts to decrease, while C' peaks appear when the field starts to rise in the case of uni-directional pulsing.

C and C' peaks decay rapidly compared with the corresponding B peaks. The C' peaks become smaller relative to the B peaks at lower frequencies. If the field strength is raised, the B peaks grow faster than the C peaks, indicating that B peaks are sensitive to the rate of growth of the applied field while C peaks are not.

Zalm and coworkers (5, 6) also report the appearance of C -like peaks under similar circumstances.

Intensity of the peaks seems to depend on the rate of growth of the field and on the time of steady field before or after field reversals (A' and B' peaks).

At very high frequencies (higher than the reciprocal of the critical time) still more complicated details appear, in particular a general decrease of the height of succeeding peaks in the green band as long as field reversals are going on (Fig. 8). This is much more conspicuous at still higher frequencies.

Finally, it should be pointed out that the patterns

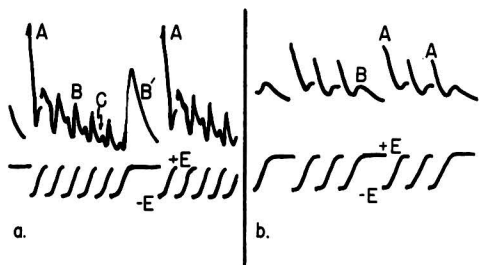


FIG. 8. Interrupted saw-tooth fields. (a) 1000 cps; (b) 1100 cps.

obtained for square pulses may be considered as simplifications of those described here inasmuch as only A -type peaks would be present.

Extinguishing effect.—If the cell is first exposed to near ultraviolet radiation and then, in addition, is placed under the influence of an electric field that is too weak to produce electroluminescence, the luminescence excited by ultraviolet radiation is diminished (14). The behavior resembles that observed for a long decay nonelectroluminescent ZnS:Cu-phosphor (15). This extinguishing effect seems to exist only in the green band. It appears with fields produced by potential differences as low as 2 volts.

INTERPRETATION

Basic assumptions.—A satisfactory basis for an interpretation must include, even if only in general terms, a description of the excitation mechanism, the luminescence processes for green and blue emission bands, and the properties of the effective internal field as distinguished from the applied external field.

Although there is no general agreement on a definite solution of the problem of the excitation mechanism, it is reasonable to assume some collision process between electrons accelerated by the field and luminescence centers. The details of such collision excitation are irrelevant as far as these considerations are concerned. The picture proposed by Curie (7) and Piper and Williams (11) (field excitation of donors, creating conduction electrons being accelerated to impact ionize or excite activators) may be accepted readily. In any case, the assumption of collision processes certainly implies that excitation must depend on the field strength, the number of electrons available for acceleration in the conduction band, and the number of centers available for excitation.

The rapid natural decay of blue luminescence, which can be described by an exponential law (Fig. 4), suggests the assumption that the blue luminescence is probably due to excitation of electrons from the ground level to some excited level within the same center, followed by an almost immediate direct transition to the ground level. Decay of the phosphor's green luminescence, however, is much slower and follows a more complicated law. The green luminescence, therefore, is probably due to some phosphorescence process with a delaying mechanism such as traps or metastable states and with transitions involving the conduction band. Similar assumptions are made by Burns (8). Also, the strong extinguishing effect observed for green luminescence only is evidence that electrons excited from green centers reach the conduction band where they can be removed by the field and made ineffective by

nonradiative transitions as considered in another case (16).

It is further assumed that green centers are excited with high efficiency, so that the number of excitable green centers strongly depends on the rate at which they are refilled. The efficiency of exciting blue centers may or may not be high. In any case, the number of excitable blue centers will remain practically unchanged because of the fast rate of refilling indicated by fast natural decay. The term "excitable center" shall indicate that the total number of centers may be much larger, but that for every field strength there may be a certain limit as to how many centers can be excited out of the total. This limit may be related to the energy level of the center.

The effective field strength in a semiconducting particle embedded in a dielectric material between metal electrodes may be expected to be different from the field applied to the electrodes. At any one instant, the effective field may be different in various regions of the phosphor particle, since strong fields are probably concentrated near the surface. One should also expect that the effective field changes in time as space charges or polarization charges build up. Thus, the field in the interior of the particle will diminish because of the polarization charges drawn to the surface by the field. If the applied field is suddenly removed after the polarization charges have accumulated, these charges themselves should create a field whose strength would decrease as the charges flow back to a neutral distribution. Therefore, if the applied field is removed or reversed faster than the polarization charges would disperse, one would expect an effective field with a maximum value shortly after application of the field reversal or removal. For slower changes of the external field, this maximum would shift to longer times. The rates of change of field and accumulation and dispersal of space charges, therefore, determine the growth and decay of the internal field.

This picture is essentially identical with ideas proposed by Kallmann (10) to explain photoconductivity experiments. He infers from his observations that at least some part of the polarization charge is trapped so that a quasi-persistent polarization of the phosphor particle is produced, which builds up and decays very slowly. Waymouth and Bitter (4) arrived at similar conclusions from electroluminescence experiments.

If the field is only removed or diminished and not reversed, the polarization charges not only provide the effective field at the removal time, but also act as an additional supply of electrons released for recombination with holes.

There is evidence that electroluminescence is restricted to small regions of the phosphor particle

(6, 17). The discussion applies to this sensitive region only. However the variation of luminescence in time is of more concern than its location.

General discussion.—The basic assumptions enumerated above appear sufficient to account for most of the observations, at least qualitatively. The general mechanism responsible for the production of peaks like those in Fig. 1 may be described as follows. At the time the field is suddenly applied or reversed, electrons in the conduction band are accelerated by the field and excite luminescence centers by some collision process. In due time, conduction electrons pile up near one surface, weakening the effective field in the interior of the particle (or its sensitive region) with a corresponding decrease of the phosphor light output. The break in decay curves at the critical time of about 0.7 msec indicates two polarization processes, a fast one and a slow one which may be identified with the piling up of electrons held either in the conduction band by the field alone or in traps producing the "persistent" polarization.

At removal of the field, the polarization charges for some time provide the field necessary for occurrence of the peaks. Similarly, at field reversals the effective field is, for the first moment, the sum of the applied field and the field of the polarization charges, after which the effective field decays again.

It is easily understood that the shape of the luminescence peaks depends on the manner of growth and decay of the internal field which itself is determined by the wave shape of the applied field. Therefore, the *B* peaks and *D* peaks in Fig. 6 to 8 are considered generally to be of the same origin as the *A* peaks, the difference in shape being due only to the difference in field shapes.

Results obtained with rectangular field pulses (Fig. 5) furnish further information that shall be used to specify the model presented here in some respect and to test its applicability.

Events leading to the blue curve of Fig. 5 may be described as follows. At some field reversal, blue centers are excited, but the excited electrons return almost immediately to their ground levels so that there is always a sufficient number of excitable centers. Decay of the blue luminescence must, therefore, be considered as being due to decay of the effective field, although the intensity may not be a direct measure of the field strength. If the field is reversed again, the situation is the same as before: a sufficient number of excitable centers and an effective field that decays from a maximum value at the time of reversal. Therefore, an intensity increase equal to that observed before is found.

For intervals shorter than the critical time, polarization charges apparently do not have sufficient time to accumulate so that the effective field con-

tributed by these charges at the time of reversal is smaller than it would have been for longer time intervals, with a corresponding decrease of the light output so that P_2 decreases as it is observed.

The typical green curve of Fig. 5 can also be understood on the basis of these general assumptions. The centers excited at some field reversal are refilled relatively slowly since the green luminescence involves trapping. A subsequent field reversal, therefore, does not find the same number of excitable centers as before, but, because one assumed the field excitation of green centers to be very efficient, all the refilled centers will be excited again. This brings the number of empty centers, the number of excited electrons, and the luminescence intensity to the same absolute value as at the previous field reversal.

While the effective field lasts, i.e., within the critical time, green decay is much faster than natural decay. This indicates an additional loss of electrons from the conduction band caused by the field. This may be due to the same kind of "field-induced non-radiative transitions" that had to be introduced (16) for the interpretation of the quenching effect of the field on a phosphor during ultraviolet excitation, but there may be still another mechanism involved. During the short time of excitation by the field pulse, the traps, which are essential for the slow natural decay, may not fill as completely as in the case of the continuous ultraviolet excitation; but, in any case, the quenching effect, for whose existence there is independent evidence, should be a contributing factor.

The critical time, interpreted here as the time necessary to pile up polarization charges, is of the same order of magnitude as the lifetime of an electron in the conduction band as determined by Curie (18). This is plausible since, on the one hand, a much shorter lifetime would make it impossible to collect a sufficient number of electrons in the cloud of drifting polarization charges; and since, on the other hand, a much longer lifetime would leave so many electrons in the conduction band that polarization charges could not be restricted to a relatively small region near the surface. In order that phenomena as described above can be observed, the indicated relation between lifetime and piling-up time should, therefore, be obeyed in the particular phosphor.

As pointed out further above, the dependence of C and C' peaks on field strength is different from that observed for B peaks. The mechanism for C and C' peaks should, therefore, be of a different kind. It is assumed that recombination of excess electrons released whenever the external field is diminished after polarization charges had time to pile up is responsible for the appearance of C peaks. Polarization charges flowing back during a time of "field

off" will be stopped suddenly when the field is applied again before they have been neutralized. They will then have an additional change of transitions, which may produce the C' peaks. At low frequencies, these peaks should disappear, as is observed, since the flow of the polarization charges has ceased before renewed field application. Both C and C' peaks should be absent for the blue band since the blue luminescence does not involve transitions from the conduction band.

The foregoing discussion provides an adequate description of the more important qualitative features of the electroluminescence patterns. Further details are considered below.

Details.—The difference between A and A' peaks in the green band is assumed to be due to the difference in numbers of excitable centers at the respective times of field reversal. For the A' peaks there is much more time for centers to be filled before the field is reversed than for the A peaks. Consequently, A' peaks are larger. There is no corresponding phenomenon for the blue peaks since the blue centers are filled much faster.

The pattern of Fig. 8' can be understood as being due to a combination of the effects previously considered, but already, without any reference to a mechanism, one should expect a decrease of the heights of subsequent B peaks in the green band since the green B peaks, according to experience, need a relatively long time to develop up to their maximum. This time is cut short while the high frequency field reversals are going on. The height of the B' peak, however, is normal again since there is sufficient time available.

The frequency dependence of the peak heights shown in Fig. 2 may also be understood on the basis of the picture developed here. Since, with increasing frequency, fewer electrons get back to the green centers before the beginning of the next half period, the number of electrons available for acceleration at this moment increases. Therefore, peaks of the blue luminescence should grow initially with frequency because of the increase in the number of accelerated electrons, but eventually the influence of the decrease of the effective field at field reversal because of the decrease of the number of polarization charges piled up during one half period must prevail. For the heights of the green peaks, it is necessary to take into account the fact that the number of filled green centers decreases with increasing frequency. This effect becomes unimportant only at extremely low frequencies. The fact that the frequency dependence follows empirically a logarithmic law is not yet understood. It may be purely fortuitous.

Finally, the general features of the electroluminescence patterns obtained with sinusoidal fields should also be governed by the processes consid-

ered here. In particular, one would expect *C*-like and *B*-like peaks, which may be distorted and shifted because of the different time characteristics of the fields. Indeed, the usually observed two peaks per half period may be identified with such peaks. The "in-phase" peaks correspond to *B* peaks, the "out-of-phase" peaks are equivalent to *C* peaks. A similar interpretation has recently been given by Curie (18).

The discussion above corroborates and supplements the general picture outlined in the previous sections, although not every detail has been treated. Thus, general aspects of the observed electroluminescence phenomena can be understood in terms of a few plausible assumptions on excitation, luminescence processes, and internal field.

ACKNOWLEDGMENTS

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Measuring Problems and Techniques at A-C Furnace Arcs¹

W. E. SCHWABE

National Carbon Research Laboratories, Cleveland, Ohio

ABSTRACT

A quantitative investigation of an a-c electric furnace arc is dependent upon measurement of the true arc voltage. The electrical resistance of an a-c arc is a function of many variables including current, arc length, electrode composition, furnace atmosphere, and temperature. Experimental procedures specially adapted to arc voltage measurement have been evolved and are described, together with a unique circuit which automatically compensates an inherent measurement error.

INTRODUCTION

The electric arc furnace and its power supply circuit form a costly tool of production and must be constructed with the rugged simplicity necessary to continuous trouble-free operation. Such construction does not provide for the wide variation of circuit parameters desirable from a research viewpoint. In a three-phase furnace, electrophysical investigations of the arc are further complicated by the interaction of the three phases.

To facilitate a practical small-scale approach to fundamental investigations of the electric furnace arc, a laboratory size, single-phase experimental arc furnace was constructed. The furnace is rated at 100 kva and was built for operation with two graphite electrodes permitting a steel capacity of 250 lb. However, to permit a more accurate control of arc length, the furnace has been adapted to single electrode operation for electrodes up to three inches in diameter. The electrical circuit is completed to the furnace shell by means of a bottom electrode. An independent electrode-positioning mechanism permits push-button control of the arc length. Power is supplied from a 440-v a-c line through a 100-kva power transformer tapped and regulated to provide a continuous variation of secondary voltage up to 280 v. Current limitation is accomplished with a number of variable resistance and inductance elements, which may be connected individually or in combination to provide the ballast desired. Fig. 1 is a schematic diagram of the experimental arc furnace circuit.

In addition to a variety of conventional electrical meters, special photographic and high-speed recording equipment is used in studies of the arc.

An extremely important parameter in an a-c electric arc furnace circuit is the arc voltage, i.e.,

the voltage drop between the electrode tip and the melt surface.

Measuring the arc voltage is a problem from both a technical and physical viewpoint. It is the objective of this paper to describe problems associated with the measurement of arc voltage, to discuss measuring techniques together with experimental results, and to propose a standard terminology for certain electrical quantities heretofore classified as arc voltage.

MEASUREMENT OF A-C ARC VOLTAGE

Measurement errors may be roughly divided into two groups as follows:

(a) external errors—introduced by the inclusion in the measurement of arc voltage, unwanted voltage drops across circuit elements adjacent to the arc; such elements include the electrode, the melt, and the furnace shell;

(b) internal errors—due to the electrophysical characteristics of arc conduction.

External errors.—An ideal measurement of arc voltage would be accomplished by connecting the leads of a suitable measuring device to the terminal points of the arc, the so-called anode and cathode spots. From a practical viewpoint such direct measurements are impossible, due to the high temperature existing inside the furnace, particularly in the arc zone. Even probe measurements, normally restricted to a short time interval, may not be applied because of the erratic travel of anode and cathode spots, characteristic of an open arc. Fig. 2 is a sequence of three photographs taken at an open arc and shows the successive half cycle locations of the arc stream occurring during each film exposure of approximately 1/30 sec (four electrical half cycles based on 60-cycle supply frequency).

In order to permit practical arc voltage measurements, meter connections have been established at the electrode clamp and on the arc furnace shell. Such measurements include the unwanted series voltage drops previously described.

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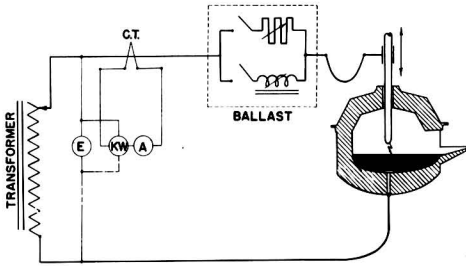


FIG. 1. Schematic diagram of experimental circuit

It is well to point out that in submerged arc furnaces the problem of measuring the arc voltage is further complicated by the contact between charge and electrode which forms parallel current paths shunting the arc, and so increasing the current through the series elements. The author's investigations have dealt primarily with the open arc, excluding detailed studies of the parallel resistance effect.



FIG. 2. Arc in a melting furnace. Three consecutive frames of a movie taken at a speed of 16 frames/sec.

The magnitude of the inherent series error has been determined for the author's circuit by lowering the electrode into the melt and measuring the short-circuit current as well as the voltage drop across the included circuit elements.

Fig. 3 is an oscillogram taken from such a test. One cycle of short-circuit current and the associated

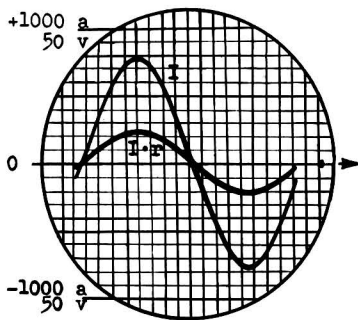


FIG. 3. Oscillogram showing the current I and the associated voltage drop $I \cdot r$ of an electrode being short-circuited with the melt.

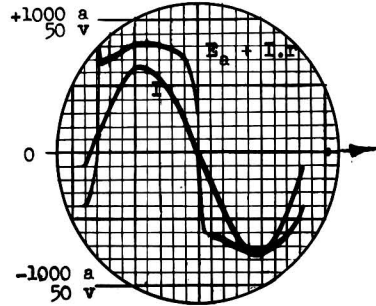


FIG. 4. Oscillogram of arc current I and arc voltage E_a including $I \cdot r$ drop.

voltage drop are plotted vs. time on the screen of a cathode-ray oscilloscope. One scale division represents 100 amp and 5 v. Peak values are 780 amp and 12 v, respectively.

An arc is established by raising the electrode from the short-circuit position, this operation being characterized by a decrease in current from its short-circuit magnitude to a value governed by the arc length and the parameters of the external circuit. Fig. 4 illustrates one cycle of current with the uncorrected arc voltage, which includes the drop previously discussed. The voltage trace is a combination of a square and a sinusoidal wave.

The error made by including the series $I \cdot r$ drop may be eliminated through a tedious point-by-point subtraction based on a knowledge of the instantaneous values of I and R . To overcome the necessity of such an operation, however, a relatively simple circuit arrangement has been developed which automatically eliminates the unwanted $I \cdot r$ drop from the recorded values of arc voltage. Both the arc and the electrode-melt-shell combination are considered to be purely noninductive resistance elements, and each in simple series circuit with the arc. Therefore, if a voltage equivalent to that across these elements, but of opposite polarity, be impressed in the metering circuit, the error is automatically canceled at every instant. The necessary voltage

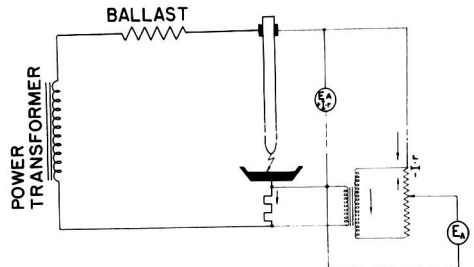


FIG. 5. Negative feedback circuit applied to measurement of arc voltage.

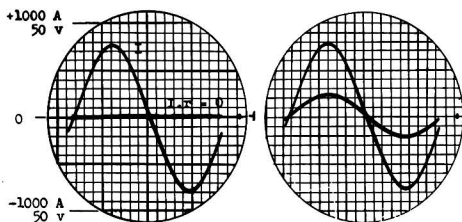


FIG. 6. Oscillograms of short circuit current and $I \cdot r$ voltage drop. *Left*, $I \cdot r$ drop cancelled; *right*, $I \cdot r$ drop present as shown in Fig. 3.

drop is readily obtained from a noninductive shunt in series with the arc, and the reversal of polarity is accomplished with a transformer. Fig. 5 illustrates the essential features of such a negative feedback circuit.²

The negative feedback circuit is very easily calibrated by establishing a short circuit between electrode and melt, and adjusting the potentiometer to precisely compensate the inherent $I \cdot r$ drop. Fig. 6 illustrates one cycle of short-circuit current and the compensated $I \cdot r$ drop. For purpose of comparison, the short circuit current and uncorrected $I \cdot r$ traces of Fig. 3 are also shown.

Fig. 7 is an arc voltage and current trace in which the $I \cdot r$ drop has been compensated by the negative feedback circuit. The uncorrected trace of Fig. 4 has been inserted for comparison. Note that the sinusoidal cap on the voltage trace of Fig. 4 has been eliminated with the negative feedback circuit, and that the voltage trace of Fig. 6 now approaches a square wave. Other changes in the voltage and current wave forms of the two oscillograms are attributed to changes in the arc during the time elapsed between the two photographs.

It is of interest at this point to call attention to the fact that in Fig. 7 peak values of both voltage and current differ in each half cycle, the voltage reaching peak values of 33 and 25 v, respectively, with current peaks of 660 and 630 amp, respectively.

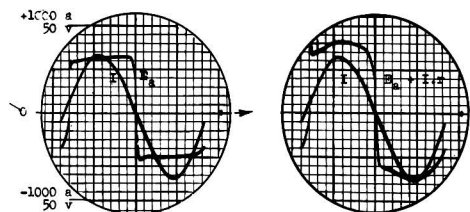


FIG. 7. Oscillograms of current I and arc voltage. *Left*, corrected arc voltage; *right*, uncorrected arc voltage as shown in Fig. 4.

² It is conceivable that this circuit be modified to compensate the true impedance drop given by $I \cdot z$, where $z = \sqrt{r^2 + x_L^2}$, in cases where the inductive component assumes significant proportions.

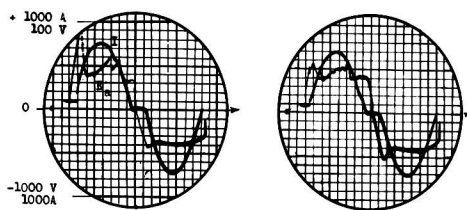


FIG. 8. Disturbance of the arc voltage during melt-down of steel. Upper half-cycles: melt = cathode; lower half-cycles: graphite-electrode = cathode.

This effect is primarily due to differences between the cathode behavior of graphite and iron, as the polarity reverses with the alternating current. During the first half cycle when the graphite is cathode, a better arc conductivity is shown by the higher current and lower arc voltage. During the succeeding half cycle the converse is true.

The arc studied in Fig. 4 and 7 was struck between a graphite electrode and a slag-covered melt. Presence of a slag on the surface of the melt has a smoothing effect on the arc voltage wave form. In the case of an arc between a graphite electrode and liquid metal in the absence of slag, the arc voltage wave form is distorted by an erratic high-frequency disturbance in the half cycle during which the melt is cathode. This disturbance also deforms the current trace. The oscillograms of Fig. 8a and b were taken at an arc struck directly to liquid steel and illustrate the effect of this disturbance on the arc voltage wave forms.

Finally, it should be mentioned that, as an alternate source, the opposing voltage for the negative feedback circuit may be obtained from the secondary circuit of a current transformer connected in the furnace circuit, and that a calculation of the required opposing voltage may be made if the circuit parameters are known. Such a calculation eliminates the necessity of conducting a short-circuit test.

This negative feedback principle is readily adaptable to measurements of arc power and resistance and may find application in the precise determination of maximum arc power occurring at optimum current as well as in automatic electrode regulating systems.

Internal errors.—Having eliminated external errors with the negative feedback circuit, calculations of arc power based on independent measurements of arc voltage and current are still in error by a varying positive quantity. Through an oscillographic analysis of individual half cycles of arc voltage and current, it was concluded that conventional voltmeters indicating either rms or average values receive a positive influence from a portion of each half cycle of voltage which does not contribute to arc power,

so that are power computations based on independent voltage and current measurements are necessarily in error.

Each half cycle of arc voltage is characterized by an initial period during which the open-circuit voltage rises to the value necessary to re-ignite the arc. As soon as the arc strikes, the voltage drops suddenly to a relatively constant value for the remainder of the half cycle. Compared with submerged arc, the open arc of an electric steel furnace is subject to a more rapid heat dissipation accompanied by a more rapid cooling of both anode and cathode spots, and so necessitating a relatively higher ignition voltage in each half cycle. The time delay until this ignition voltage is reached varies with the nature of the circuit. In a circuit containing little reactance, the time delay between zero voltage and ignition voltage is increased, whereas the phase displacement between current and voltage due to the inductance in a conventional arc furnace circuit promotes arc re-ignition by delivering an additional voltage of self-induction, $L di/dt$, which reaches its maximum when the current is near zero.

The oscillograms of Fig. 9 were taken at an arc circuit containing very little inherent reactance and demonstrate two extremes of ignition peak and correlated time delay. Fig. 9a shows the arc voltage and current at the beginning of a half cycle. The arc was struck between a graphite electrode and a slag-covered melt. Some time elapses before the current increases; this represents the ignition delay and, in this case, may be expressed as approximately five electrical degrees. Fig. 9a was taken at a short arc, the graphite electrode having been cathode in this particular half cycle. When the input voltage, governed by its sinusoidal variation, reaches the arc ignition value of approximately 15 v, a current flows.

In this case of short arc, there is no clearly defined ignition peak, and the arc voltage actually rises from its ignition value to remain almost constant

at twenty volts. This phenomenon is attributed to the superior conductivity of the short arc. In Fig. 9b the arc length has been increased, the other circuit parameters having been unchanged. In this case, the ignition delay is almost 45 electrical degrees, and the current flows only when an ignition voltage of about 90 v is reached. When the current flow is established, the voltage drops from its ignition value to 60 v and remains almost constant.

The time portion of the arc voltage from its intersection with the zero axis to the ignition peak is essentially the open-circuit voltage, and does not contribute significantly to the power of the arc. For this reason, it is referred to as the *passive* arc voltage. The time portion of the arc voltage during which a current flows has been designated the *active* arc voltage.

It is apparent that a conventional voltmeter responds to the passive as well as to the active arc voltage and that its over-all indication is higher than it should be. Arc power computations based on independent measurements of arc voltage and current are, therefore, in error by this varying positive value.

It should also be noted that in the case of prolonged ignition delay, the current does not reach its maximum at 90 electrical degrees as with a sine wave, but somewhat later. Although Fig. 9a and b illustrate the usual extremes of ignition delay, occasional delays of 55-60 electrical degrees have been observed.

Fig. 10 is a simplified reconstruction of another arc voltage trace. The input voltage in this case is 50 v rms (70.7 v peak). The ignition delay is 30 electrical degrees, and the ignition voltage is 35 v. The active arc voltage is 23.3 v and remains constant from 30 electrical degrees to 160 electrical degrees

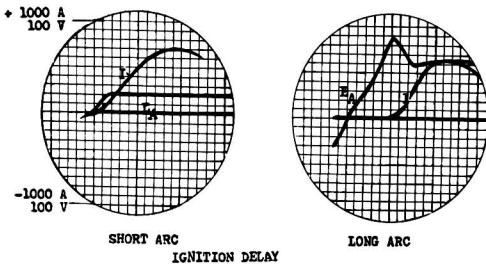


FIG. 9. Oscillograms showing parts of one half-cycle of arc current I and corrected arc voltage E_a . Left, short arc, current flow starts immediately; right, long arc, current flow delayed.

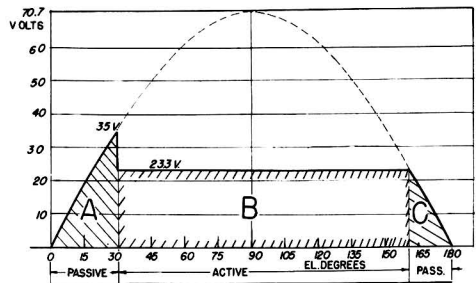


FIG. 10. Reconstruction of a typical arc voltage half-cycle. Areas A and C are passive; area B is active. Calculated meter readings of rms and average values:

Meter type	Indication	Active arc voltage (B)	Apparent arc voltage (A + B + C)	Error %
Dynamometer or thermo.	RMS	19.3	21.8	+13
Rectifier	Avg	16.4	19.3	+18

at which point it breaks down to zero. Areas A and C are passive, only area B being active in contributing to arc power.

The average and rms values for the entire voltage curve as well as for the active portion have been calculated. Both sets of calculations are based on a full half cycle (180 electrical degrees). The results of the calculations are listed in the table of Fig. 10 and indicate errors of +13 and +18% in the conventional meter readings of rms and average arc voltage, respectively. The error values calculated in this particular case are only indicative, since they apply only to the particular half cycle in question, although they do demonstrate the existence of a very considerable error.

MEASUREMENT OF ACTIVE A-C ARC VOLTAGE

It is apparent from the foregoing discussions that the active arc voltage for any short period may be measured by oscillographic means, provided that the negative feedback principle is applied. A much more desirable arrangement would provide a continuous rms meter reading of the active arc voltage. An intermediate solution may be based upon the ratio of watts to rms amperes to give the effective rms voltage. It can be assumed that the arc is a pure resistance, so that the power factor is unity. A major disadvantage of this wattmeter-ammeter method lies in the fact that two simultaneous readings are necessary. These readings are difficult to obtain, especially at melting furnaces during the melt down period, when current and arc power fluctuate rapidly.

To overcome the necessity of making two simultaneous readings, it is conceivable that the watt-

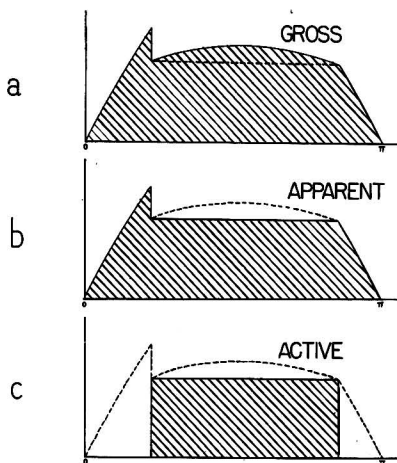


FIG. 11. Schematic definition of gross, apparent, and active a-c voltage.

meter and ammeter indications might be combined in a single instrument so calibrated that its resultant continuous indication is watt/amp, or active rms arc voltage. Such a circuit has not been developed. A relatively simple electronic circuit is also conceivable, by means of which the voltmeter circuit is only closed when current is flowing.

The ratio of the active part of the arc voltage to the apparent arc voltage expressed as a percentage may be designated an *arc form factor*. Having measured the active and apparent arc voltage by means of the previously described wattmeter-ammeter method and an electrodynamic voltmeter, respectively, arc form factors of 80–90% at an open arc between a graphite electrode and steel have been determined.

Lower values between 60 and 70% were found at arcs with a more pronounced rectifying effect.

It is essential to keep in mind that such meter readings average the conditions of both half waves.

DISCUSSION

As previously stated, electrophysical investigations of the electric furnace arc conducted at producing installations have many practical limitations. Therefore, small-scale investigations utilizing an experimental furnace have been undertaken in preliminary studies of this important arc.

In the past, a considerable obstacle to the efficient collection of comparison data has been a certain ambiguity of terms commonly used in reference to the electrical operating characteristics of industrial arc furnaces. Clarification and standardization of these terms is considered to be of importance with respect to continued investigations of the complex physics of the electric furnace arc.

It is pointed out that the indications or reactions of many conventional electrical or electromechanical devices depend to some degree on the arc voltage as an activating impulse, and are positively influenced by both external and internal errors as described in the foregoing sections. The following definitions of terms related to a-c arc voltage are offered as a step toward a more thorough understanding of the electric furnace arc.

1. Gross A-C Arc Voltage

The alternating potential difference existing between the two nearest convenient points of the arc furnace circuit including the arc. This includes the voltage drop between the anode and cathode spots as well as that across resistance elements external to the arc, e.g., the potential difference between electrode clamp and furnace shell as measured by a voltmeter indicating rms or average values (see Fig. 11a).

2. *Apparent A-C Arc Voltage*

The alternating potential difference existing between the anode and cathode spots of an a-c arc. This can be measured either by connecting adequate probe contacts directly to the anode and cathode spots or, more practically, by making connections at external points and correcting the indication by means of a feedback circuit (see Fig. 11b).

3. *Active A-C Arc Voltage*

That portion of each individual half cycle of ap-

parent arc voltage contributing to arc power. The rms value of active arc voltage can be calculated from simultaneous wattmeter and ammeter readings (see Fig. 11c).

4. *Arc Form Factor*

The per cent ratio between the active and the apparent arc voltage.

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

Diffusion of Hydrogen and Deuterium in High Purity Zirconium¹

EARL A. GULBRANSEN AND KENNETH F. ANDREW

Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania

ABSTRACT

Kinetics of the reaction of zirconium with pure hydrogen and deuterium was studied for 60°–250°C, H₂ pressures of 1.1–5.0 cm Hg, and composition range Zr–ZrH_{1.70}, using a vacuum microbalance method. The reaction was shown to be diffusion-controlled with diffusion occurring from a surface of constant concentration into a heterogeneous system.

The diffusion equation was solved for these conditions using the method originally developed by Neuman and recently applied by Wagner to this type of problem. Average concentration according to this view is given by

$$\bar{C} = 2.845 \frac{D^{1/2} t^{1/2}}{h}$$

where D is diffusion coefficient in cm²/sec, t is time in seconds, and h is specimen thickness in centimeters.

Plots of \bar{C} vs. $t^{1/2}$ show this relationship to hold over wide variations in time, temperature, pressure, and specimen thickness. Diffusion coefficients were calculated and when plotted against $1/T$ on a logarithmic plot gave a heat of activation of 11,400 cal/mole. The corresponding entropy of activation was 2.7 cal/mole/°C.

The following equation expresses data for diffusion of hydrogen in zirconium:

$$D = 1.09 \times 10^{-3} e^{-11,400/RT} \text{ cm}^2/\text{sec}$$

For the composition range of Zr to ZrH_{1.4}, experimental data fit the proposed explanation for the reaction. At higher compositions, deviations were observed.

Diffusion of deuterium in zirconium was also studied and data found to fit the equation:

$$D_{D_2} = 0.73 \times 10^{-3} e^{-11,400/RT} \text{ cm}^2/\text{sec}$$

The relationship between the diffusion coefficient of hydrogen and deuterium was found to be 1.5. The theoretical value should be $\sqrt{2}$.

The diffusion mechanism proposed was verified by experimental results.

INTRODUCTION

Much of the work on the reaction of zirconium with hydrogen was reviewed by Smith in 1948 (1) and by Gulbransen in 1954 (2). Two studies have been made of the kinetics of the reaction with hydrogen. Gulbransen and Andrew (3) studied the rate of hydriding between 200° and 300°C using high purity metal and a source of highly purified hydrogen. Although some kinetic data were obtained, the rate of reaction was difficult to reproduce and appeared to be sensitive to pretreatment and to surface films. Since the initial surface oxide film was not removed and its importance was not recognized at that time, these kinetic results must

be interpreted in terms of an oxide-contaminated surface.

Bernstein and Cubicciotti (4) studied the permeation of zirconium by hydrogen at 545°–920°C. Again, results were difficult to reproduce, and evidence for a contaminating film was observed in all experiments.

Recent studies by Gulbransen and Andrew (5) showed that the room temperature surface oxide film has a remarkable inhibiting effect on rate of hydriding. Unless great care was taken to remove the initial oxide film and to purify the hydrogen, the rate of hydriding was limited by a surface reaction.

Since the mechanism of hydriding of zirconium may involve one or more diffusion processes, precise information on the phase diagram of zirconium-hydrogen alloys is required. Although Hägg (6)

¹ Manuscript received March 29, 1954. This paper was prepared for delivery before the Chicago Meeting, May 2–6, 1954.

studied the system earlier and showed the existence of several hydride phases, the ranges of homogeneity of these phases were not established.

To supplement this work, Gulbransen and Andrew (7) determined ranges of homogeneity of several phases from thermodynamic studies and from x-ray diffraction studies. In brief, for temperatures below 500°C, the ϵ -phase of Hägg was shown to have a composition range of $\text{ZrH}_{1.965}$ to $\text{ZrH}_{1.64}$, while the δ -phase has a range from $\text{ZrH}_{1.56}$ to $\text{ZrH}_{1.40}$. A two-phase region of α - and δ -phases exists for all compositions between zirconium saturated with hydrogen in solid solution and $\text{ZrH}_{1.40}$. At 250°C, the maximum temperature used in this work, the solubility of hydrogen in zirconium corresponds to the composition $\text{ZrH}_{0.001}$ (8).

With this new information on the phase diagram, and with techniques available for removing the initial surface oxide film and for purifying hydrogen, it was possible to study the mechanism of the reaction of pure hydrogen with a clean zirconium surface.

ANALYSIS OF DIFFUSION PROBLEMS

Wagner (9) has discussed the general problem of diffusion in binary systems of more than one phase. From a mathematical point of view this problem was similar to that of melting or solidification in which one substance changes into another with emission or absorption of heat. The common feature of these problems was the existence of a moving surface of separation between two phases, at which material or heat was being transferred. The original solution of the heat problem was due to Neuman and was presented in a book by Carslaw and Jaeger (10).

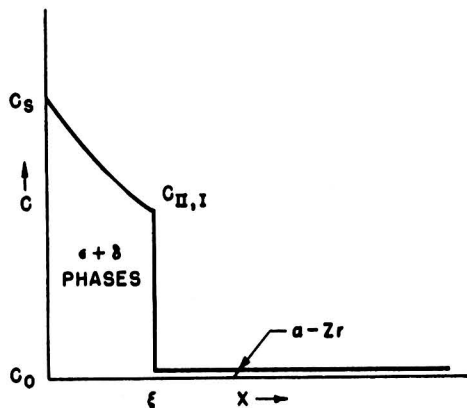


FIG. 1. Diffusion picture, hydrogen in zirconium (after Wagner). $t > 0$; $c_s = \text{ZrH}_{1.965}$; $c_{II,I} = \text{ZrH}_{1.40}$; $c_0 = \text{ZrH}_{0.001}$ at 250°C.

General picture.—Fig. 1 shows the analysis given by Wagner (9) for diffusion from a surface into a heterogeneous system for a flat plate. c_s is the surface concentration at $x = 0$, c_0 is the concentration at time $t = 0$, and $c_{II,I}$ is the concentration in phase II at the interface ξ with phase I. Diffusion proceeds from the surface in the homogeneous phase II. At time t the region of phase II extends from $x = 0$ to $x = \xi$.

Since hydrogen reacts with zirconium to form two hydride phases in addition to dissolving in α -zirconium, the validity of the diffusion picture shown in Fig. 1 may be questioned. However, the ϵ and δ hydride phases for most purposes can be considered as one phase, since their ranges of homogeneity are nearly continuous (7) and since their crystal structures are similar. The effect of solution of hydrogen in the metal is negligible since the solubility at 250°C is of the order of $\text{ZrH}_{0.001}$ (8).

General solution.—The following equation governs the diffusion process:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (\text{I})$$

Here the diffusion coefficient, D , is assumed to be independent of concentration. The boundary condition is

$$c = c_s \text{ at } x = 0 \text{ and } t > 0 \quad (\text{II})$$

At the interface $x = \xi$ the concentration of diffusing species in phase II is that relating to the equilibrium value between phases I and II.

$$c = c_{II,I} \text{ at } x = \xi \quad (\text{III})$$

When the interface is displaced by $d\xi$ for a time dt , the quantity $[c_{II,I} - c_0] d\xi$ of hydrogen must be supplied from the region $x < \xi$. Thus,

$$[c_{II,I} - c_0] d\xi = D dt \left(\frac{\partial c}{\partial x} \right)_{\xi=0} \quad (\text{IV})$$

A particular solution of equation (I) for boundary condition (II) is

$$c = c_s - B \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right), \text{ for } 0 < x < \xi \quad (\text{V})$$

Here, B is a constant and erf is the error function.

Wagner (9) assumes as does Neuman (10) that the plane of discontinuity is shifted proportional to $t^{1/2}$. Thus,

$$\xi = \gamma \sqrt{Dt} \quad (\text{VI})$$

Here, γ is a dimensionless parameter.

Substituting, one obtains

$$c_s - c_{II,I} = B \operatorname{erf}(\gamma) \quad (\text{VII})$$

$$c_{II,I} - c_o = \frac{B}{\sqrt{\pi}} \exp(-\gamma^2) \quad (\text{VIII})$$

Eliminating B , one has

$$\frac{c_s - c_{II,I}}{c_{II,I} - c_o} = \sqrt{\pi} \gamma e^{\gamma^2} \operatorname{erf} \gamma \quad (\text{IX})$$

γ can be found from equation (IX) and B from equations (VII) and (VIII).

D is usually found by observing the displacement ξ and by the use of equation (VI). However, if the reaction is followed by a weight gain method, D must be obtained from the average concentration in the sample as a function of time.

Solution for weight gain method.—Let \bar{c} be the average concentration in phase II, $o < x < \xi$. Then,

$$\begin{aligned} \bar{c} &= \frac{1}{\xi} \int_0^{\xi} c(x, t) dx \\ &= \frac{1}{\xi} \int_0^{\xi} \left[c_s - B \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right] dx \quad (\text{X}) \end{aligned}$$

$$= \frac{1}{\xi} \left[c_s \xi - B \int_0^{\xi} \operatorname{erf} \frac{\gamma x}{\xi} dx \right] \quad (\text{XI})$$

Integrating,

$$\bar{c} = c_s - B \operatorname{erf} \gamma + \frac{B}{\gamma\sqrt{\pi}} (1 - e^{-\gamma^2}) \quad (\text{XII})$$

This shows that \bar{c} is independent of t .

Substituting (VII) and rearranging,

$$\frac{\bar{c} - c_{II,I}}{c_s - c_{II,I}} = \frac{1 - e^{-\gamma^2}}{\gamma\sqrt{\pi} \operatorname{erf} \gamma} \quad (\text{XIII})$$

Using this analysis, equations (IX) and (XIII) are plotted as a function of γ . From the plot of equation (IX) a value for γ is obtained and from a plot of equation (XIII) and this value of γ , a value for

$$\frac{(\bar{c} - c_{II,I})}{(c_s - c_{II,I})}$$

can be obtained.

From these plots $\gamma = 0.425$ and

$$\frac{\bar{c} - c_{II,I}}{c_s - c_{II,I}} = 0.485$$

Now an expression can be written for the average concentration \bar{C} over the whole specimen:

$$\bar{C} \frac{h}{2} = \bar{c}\xi + c_o \left(\frac{h}{2} - \xi \right) \quad (\text{XIV})$$

Here, $h/2$ is the half thickness and c_o the solubility of hydrogen in α -Zr. For temperatures of 250°C and lower, c_o has a value of 0.001 or less in terms of the ratio H/Zr and is, therefore, negligible.

Substituting equation (VI) and (XIV) and the values for γ and \bar{c} ,

$$\bar{C} = 2.845 \frac{D^{1/2} t^{1/2}}{h} \quad (\text{XV})$$

For the 0.0127 cm specimens, this equation becomes

$$\bar{C} = 224 D^{1/2} t^{1/2} \quad (\text{XVI})$$

and for the 0.0508 cm specimens,

$$\bar{C} = 56 D^{1/2} t^{1/2} \quad (\text{XVII})$$

In deriving equation (XV) from (XIV) it is assumed that c_s is constant and independent of pressure. Phase diagram studies by Gulbransen and Andrew (7) show that c_s has a value of 1.965 in terms of the ratio H/Zr, and for temperatures of 250°C and lower, c_s is independent of pressures of the order of 1 cm Hg and higher.

Testing of the mechanism of the reaction.—The reaction mechanism upon which equation (XV) is based can be tested experimentally. First, plots of \bar{C} vs. $t^{1/2}$ can be used to test the square root of time relationship. Second, use of different thicknesses of samples tests the validity of equation (XV). Third, use of both hydrogen and deuterium having different diffusion coefficients gives an additional way of testing equation (XV). Fourth, the analysis assumes a constant value for c_s . The effect of pressure, therefore, should be negligible. Fifth, a plot of $\log D$ vs. $1/T$ should give a straight line and a reasonable heat of activation. Sixth, the entropy of activation of the diffusion process should have a value near zero or slightly positive.

EXPERIMENTAL

A vacuum microbalance was used to determine the rate of reaction of hydrogen with the metal. Its construction and use has been described in previous publications (11, 12). The sensitivity of the balance was 1.25 divisions (0.00125 cm) per microgram for the 0.05 g sample, and the weight change was estimated to $\frac{1}{4}$ of a division (0.20×10^{-6} g).

A mullite furnace tube sealed directly to the Pyrex glass system contained the specimen. The vacuum behavior of this system has been described (13). Special precautions necessary for the study of zirconium have also been described (5). In all experiments described here, the system and specimen were pumped for at least 15 hr to minimize contamination of the gas atmosphere by degassing of the walls of the vacuum system.

Specimens were sheets of zirconium 0.0127 and 0.050 cm thick. Two weights of specimen were used, 0.0486 g or 0.4995 g. The larger specimens were used for experiments at 60°–100°C where the

TABLE I. Analysis of zirconium samples

	Footc Zr typical wt %
Si	0.01
Fe	0.04
Al	0.01
Cu	<0.01
Ti	0.03
Mn	<0.001
Ca	0.01
Mg	<0.003
Pb	<0.001
Mo	<0.001
Ni	0.01
Cr	0.001
Sn	0.001
W	<0.001
N	<0.01
O	<0.01
H	<0.02
C	<0.001
Hf	2.40

amount of reaction was small, while the smaller specimens were used where a large reaction with hydrogen was expected.

Pure hydrogen or deuterium was prepared by diffusing the purified electrolytic hydrogen or high purity grade of deuterium (99.66% D₂) through a palladium tube (11). To minimize contamination the gas was prepared immediately before use.

High purity iodide zirconium was obtained from Foote Mineral Company. The analysis is given in Table I. All specimens were given an abrading and cleaning treatment as previously described (5). They were placed in turn on the balance, and the tube sealed off. The specimen and vacuum system was pumped for 15 hr or longer. Before reacting with hydrogen, each sample was heated to 700°C in high vacuum for 1-2 hr.

RESULTS AND DISCUSSION

General

Fig. 2 shows a series of weight gain vs. time curves for the hydriding of zirconium at 150°-250°C and for a hydrogen pressure of 5 cm Hg. A new specimen was used for each experiment. For the area and weight of the specimens, a weight gain of about 715 $\mu\text{g}/\text{cm}^2$ corresponds to a concentration of $\text{ZrH}_{1.965}$. In several of the experiments shown in Fig. 2, this concentration was achieved. No visual evidence was found for the presence of an oxide film after concluding the experiment.

Fig. 3 shows a similar series of curves for 60°-125°C. The curves were of similar shape to those of Fig. 2. However, the maximum concentration at-

tained in these experiments for one hour of reaction was $\text{ZrH}_{0.2}$.

There is no evidence of an induction period which suggests that the surface was free of oxide film and that the reaction is diffusion-controlled. Previous studies (5) have shown that very thin oxide films (a) exert a strong inhibiting influence on the hydrogen reaction, (b) were responsible for the observed induction period of the reaction, and (c) explain many of the supposedly inert characteristics of the metal to reaction with hydrogen.

Rate law correlation.—To test the mechanism of reaction, the average concentration \bar{C} was plotted against the square root of time according to equation (XV). Fig. 4 shows this type of plot for the 250° and 175°C experiments. The 250°C data follow a straight line relationship up to a concentration corresponding to an H/Zr ratio of 1.60 or the limit of the two-phase region. The 175°C data show a straight line relationship to the concentration limit of the experiment, namely, a value of H/Zr of 0.86.

Fig. 5 shows similar plots for the 60° and 100°C experiments. Although only the initial stage of the reaction was studied, straight line relationships were

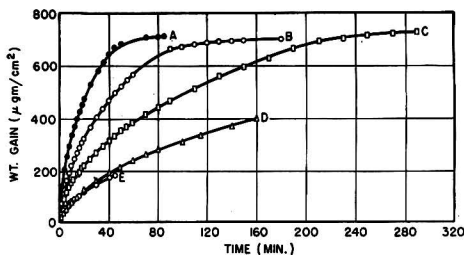


FIG. 2. Effect of temperature on hydriding zirconium. Curve A, 250°C, 5 cm of Hg of H₂; curve B, 225°C, 5 cm of Hg of H₂; curve C, 200°C, 5 cm of Hg of H₂; curve D, 175°C, 5 cm of Hg of H₂; curve E, 150°C, 5 cm of Hg of H₂.

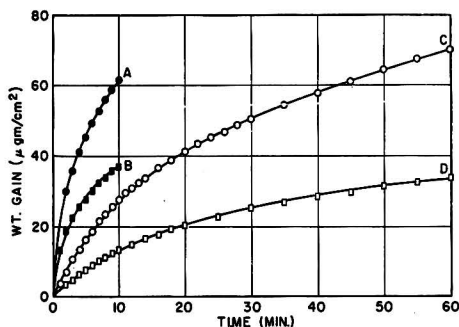


FIG. 3. Effect of temperature on hydriding zirconium. Curve A, 125°C, 2.3 cm of Hg of H₂; curve B, 100°C, 2.4 cm of Hg of H₂; curve C, 80°C, 2.4 cm of Hg of H₂; curve D, 60°C, 2.4 cm of Hg of H₂.

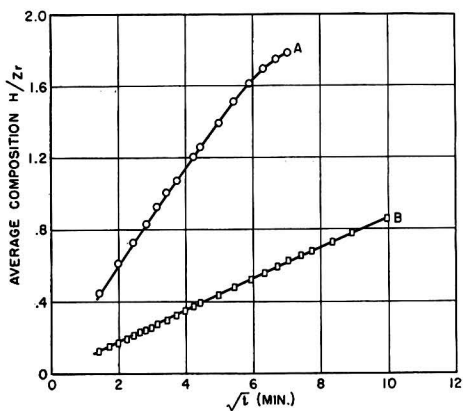


FIG. 4. Effect of temperature on hydriding zirconium. Curve A, 250°C, 5.0 cm of Hg of H₂; curve B, 175°C, 5.0 cm of Hg of H₂.

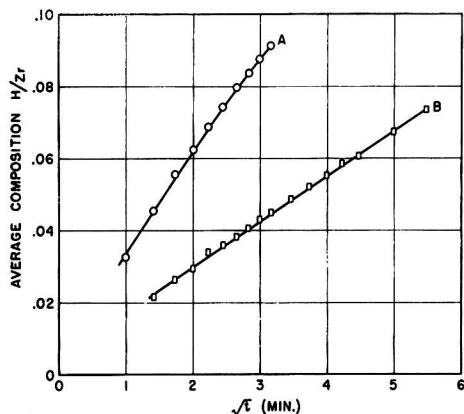


FIG. 5. Effect of temperature on hydriding zirconium. Curve A, 100°C, 2.4 cm of Hg of H₂; curve B, 60°C, 1.4 cm of Hg of H₂.

found. Thus equation (XV) adequately describes the time behavior, including the assumption made by Wagner on the movement of the interface between phases.

Effect of pressure.—Fig. 6 shows \bar{C} vs. $t^{1/2}$ plots of the data for two experiments at 225°C in which the pressure was varied from 1.1 to 5.0 cm of Hg. Slopes of the two plots were identical. The difference between the curves was due to the fact that the buoyancy correction² was not applied to the data. Hence the effect of pressure on the rate of hydriding was negligible, and the surface concentration c_s was essentially ZrH_{1.965}. This conclusion was also supported by thermodynamic evidence (7).

Effect of sample shape.—According to equation

² This correction was a result of thermal convection currents set up in the furnace tube. It could be evaluated from the final vacuum reading.

(XV) the sample thickness, h , affects the slope of the \bar{C} vs. $t^{1/2}$ plot by the factor $1/h$. Fig. 7 shows a comparison of this type of plot for two thicknesses of metal, 0.0127 and 0.0508 cm. The effect of h on the plots was that predicted by equation (XV).

Calculation of Diffusion Coefficients

Equation (XV) was used to calculate diffusion coefficients from the \bar{C} vs. $t^{1/2}$ plots. These are summarized in Table II. Fig. 8 shows these data on a $\log D$ vs. $1/T$ plot, and from the slope a heat of activation of 11,400 cal/mole was calculated. Data for samples of different thicknesses were included. D_o was calculated from the equation

$$D = D_o e^{-\Delta H^*/RT} \quad (\text{XVIII})$$

Here, D_o was the value of D at infinite temperature, and ΔH^* was the heat of activation of diffusion. The values of D_o were tabulated and an average value of 1.09×10^{-3} was calculated. The data could be represented by

$$D = 1.09 \times 10^{-3} \times e^{-11,400/RT} \text{ cm}^2/\text{sec} \quad (\text{XIX})$$

The value of 11,400 cal/mole for the heat of activation of diffusion for hydrogen in zirconium

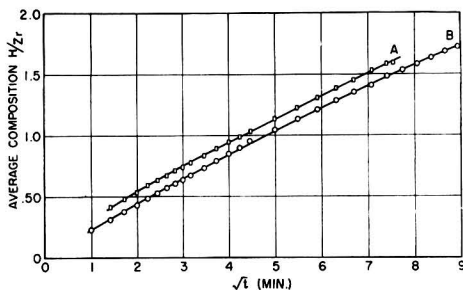


FIG. 6. Effect of pressure on hydriding zirconium. Curve A, 225°C, 5 cm of Hg of H₂; curve B, 225°C, 1.1 cm of Hg of H₂.

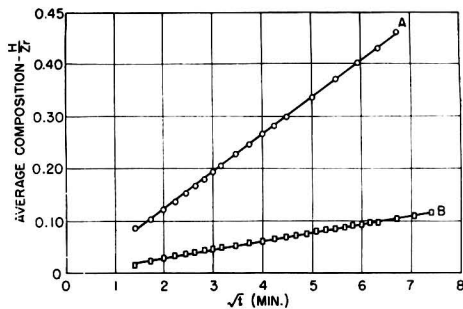


FIG. 7. Effect of sample thickness on hydriding zirconium. Curve A, 0.0127 cm thick, 150°C, 2.4 cm of Hg of H₂; curve B, 0.0508 cm thick, 150°C, 5.0 cm of Hg of H₂.

TABLE II. Diffusion data hydrogen in zirconium

$t^\circ\text{C}$	$1/T \times 10^3$	D_{avg} cm^2/sec	D_0 cm^2/sec
60	3.0021	4.60×10^{-11}	1.341×10^{-3}
80	2.832	7.09×10^{-11}	0.784×10^{-3}
100	2.680	2.54×10^{-10}	1.178×10^{-3}
120	2.544	3.25×10^{-10}	0.705×10^{-3}
125	2.512	6.43×10^{-10}	1.144×10^{-3}
150	2.360	1.625×10^{-9}	1.26×10^{-3}
175	2.232	2.470×10^{-9}	0.876×10^{-3}
200	2.114	6.02×10^{-9}	1.099×10^{-3}
225	2.008	1.33×10^{-8}	1.33×10^{-3}
250	1.912	2.215×10^{-8}	1.217×10^{-3}
			avg 1.09×10^{-3}

appears to be reasonable since value heats of activation of 5,740–10,100 cal/mole have been observed (14) for the diffusion of hydrogen in palladium. The most reliable work on diffusion of hydrogen in palladium gave a value of 5,740 cal/mole (15, 16).

Calculation of Entropy of Activation

One of the best ways to check on diffusion results is to make an approximate calculation of the entropy of activation using the classical theory of diffusion as restated by Zener (17). According to this theory, D_0 is given by the expression

$$D_0 = ga^2\nu e^{\Delta S^*/R} \quad (\text{XX})$$

Here, a is the distance between sites for diffusion, ν is the frequency of vibration along the path of the

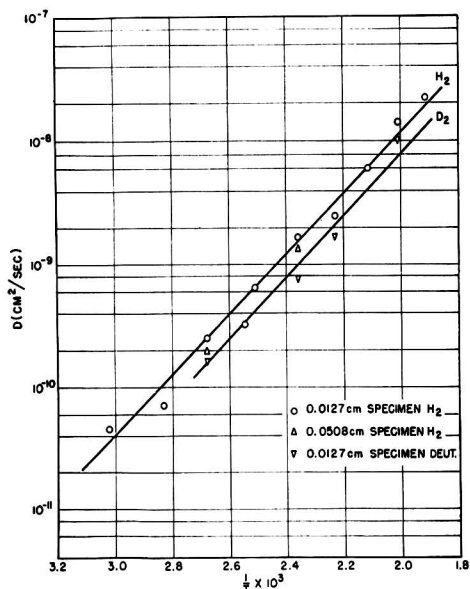


FIG. 8. D vs. $1/T$ log plot (60° – 250°C). $\Delta H = 11,400$ cal/mole; $P = 1.1$ – 5.0 cm of Hg of gas.

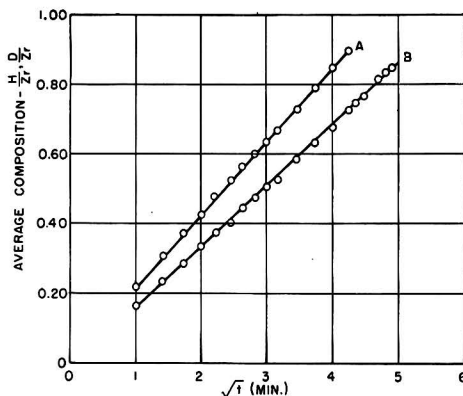


FIG. 9. Comparison of reaction of hydrogen and deuterium with zirconium. Curve A, H_2 , 225°C , 1.1 cm of Hg; curve B, D_2 , 225°C , 1.8 cm of Hg.

TABLE III. Diffusion data deuterium in zirconium

$t^\circ\text{C}$	$1/T \times 10^3$	D , cm^2/sec	D_0 , cm^2/sec
100	2.680	1.62×10^{-10}	7.5×10^{-4}
150	2.360	7.70×10^{-10}	6.0×10^{-4}
175	2.232	1.64×10^{-9}	5.8×10^{-4}
225	2.008	1.023×10^{-8}	10.0×10^{-4}
			D_0 avg = 7.3×10^{-4}

diffusion, ΔS^* is the entropy of activation of diffusion, and g is a constant determined by the geometry of the particular processes of diffusion.

In many diffusion problems the experimentally determined values include entropy and heat of activation terms for the process of forming the defects by which diffusion occurs. For the case of hydrogen in metals, such as zirconium, the tetrahedral sites in the hydride structures are already available for diffusion. Therefore, diffusion of hydrogen in the hydride structures should involve only the entropy and heat of activation terms for diffusion. According to theory, the entropy of activation should have slightly positive values.

The frequency of vibration of hydrogen atoms in the equation has been evaluated from entropy of solution data which will be discussed in a future paper. A value for ν of 4×10^{13} vibrations/sec was found. The distance a between tetrahedral sites in the δ -phase was 2.39 \AA .

To evaluate the constant g , the diffusion of hydrogen atoms or ions is assumed to occur through the movement of unoccupied tetrahedral sites. g is evaluated by calculating the probability P_i of an unoccupied site occurring next to a particular hydrogen atom or ion. The probability varies from a value of $\frac{2 - 1.965}{2}$ at the surface to a value of

$\frac{2 - 1.4}{2}$ at the interface $c_{II,I}$. The geometrical mean of these values is 0.072. Since $g = \frac{1}{6} \sum P_i$, $g = 0.012$. Substituting the values of D_0 , g , a^2 and ν , $\Delta S^* = +2.7$. This value is in agreement with theoretical predictions of Zener (17).

Diffusion of Deuterium

The diffusion of deuterium in zirconium was studied at 100°, 150°, 175°, and 225°C. Weight gain vs. time curves were similar to those seen in Fig. 2 and 3. Fig. 9 shows a comparison of \bar{C} vs. $t^{1/2}$ plots for hydrogen and for deuterium diffusing into the metal at 225°C. A straight line relationship was found for both gases.

Diffusion coefficients are summarized in Table III and plotted in Fig. 8. Although the data were somewhat scattered, the temperature dependence was the same as that found for the case of hydrogen, so the heat of activation for the diffusion process was the same for both gases. Calculated D_0 values for hydrogen and for deuterium were 1.09×10^{-3} and 7.3×10^{-4} , respectively. Therefore, the ratio of D_{H_2}/D_{D_2} was independent of temperature and approximately equal to 1.5.

Jost and Widman (15, 16) observed a ratio of 1.3 for D_{H_2}/D_{D_2} . Using the transition state theory of diffusion, they show that the effect of the mass of the diffusing specie was in the frequency term in the expression for the diffusion coefficient, the frequency of vibration being proportional to $1/\sqrt{m}$ or $1/\sqrt{2}$. Thus, the simple theory gives a ratio of D_{H_2}/D_{D_2} of 1.41. This compares with the experimental value of about 1.5.

A similar analysis could be made using the classical theory of diffusion as expressed in equation (XIX). The major effect appears to be that of mass on frequency of vibration along the path for reaction. Considering the scattering of experimental results, the diffusion of deuterium in zirconium is adequately explained by equation (XV) with the effect of mass on the frequency of vibration of the particular diffusing specie explaining the ratio of D_{H_2}/D_{D_2} .

Limit of Application of Diffusion Equation

Equation (XV) was derived on the basis of the diffusion of hydrogen from the surface through the ϵ and δ hydride phases to form new δ -phase. It was

assumed in the derivation that the plane of discontinuity was shifted proportional to $t^{1/2}$. At some value of the average concentration \bar{C} , the planes of discontinuity meet at the distance $h/2$. Equation (XIV) was used to calculate \bar{C} for this condition, and a value of 1.67 was obtained. Fig. 4 shows a plot of \bar{C} vs. $t^{1/2}$ for the hydrogen reaction at a temperature of 250°C. A straight line was found for concentrations up to 1.6–1.7. This agrees with the prediction of the equation.

ACKNOWLEDGMENT

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

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High Temperature Crystal Structure of Thorium¹

PREMO CHIOTTI

Ames Laboratory, Atomic Energy Commission, Iowa State College, Ames, Iowa

ABSTRACT

High temperature x-ray diffraction patterns and electrical resistivity measurements show that thorium of 99.8% purity transforms from face-centered cubic to body-centered cubic on heating to $1400 \pm 25^\circ \text{C}$. At 1450°C the lattice constant of body-centered cubic thorium is $4.11 \pm 0.01 \text{ \AA}$. The extrapolated lattice constant of face-centered cubic thorium at the same temperature is $5.180 \pm 0.005 \text{ \AA}$. The lattice constant of the metal used is $5.089 \pm 0.001 \text{ \AA}$ at room temperature. The transformation temperature is rapidly increased as the amount of carbon in the metal is increased. Zirconium has the opposite effect in that small amounts of it are very effective in lowering the temperature at which the transformation begins.

INTRODUCTION

Thorium at ordinary temperatures has a close-packed face-centered cubic structure. In an earlier investigation (1) some resistance measurements on thorium in the temperature range between 750° and 1700°C gave evidence of a possible allotropic transformation. At about the same time, an investigation of the thorium-zirconium system by Carlson (2) indicated that a complete series of solid solutions is formed between these two elements at elevated temperatures. Since zirconium is body-centered cubic at temperatures above 865°C , the results obtained by Carlson can be explained more satisfactorily on the supposition of the existence of a body-centered cubic form for thorium. In order to resolve this question, further resistance measurements were made and x-ray diffraction patterns were taken in the temperature range in question.

EXPERIMENTAL METHODS

The change in electrical resistance with temperature of thorium was measured over a temperature range of 750°C to its melting point. The method employed and apparatus used have been described in detail elsewhere (3). In this method, a specimen approximately a quarter-inch in diameter and four inches long is clamped between two water-cooled copper electrodes and is heated under vacuum or in an inert atmosphere to various temperatures by passing a 60-cycle alternating current through it. Two thin thorium wires are spot welded one centimeter apart near the middle of the bar where the

temperature is reasonably uniform. The potential developed between these two leads is balanced against the output of a current transformer whose primary is connected in series with the specimen. Since the output of the current transformer is proportional to the current through the primary, and the potential developed across the one-centimeter length of the specimen is the product of the same current and specimen resistance, the change in resistance with temperature is measured directly. Essentially, this is an alternating-current potentiometric null-point method. In order to balance one alternating voltage against another, it is necessary that the two voltages be of identical wave form and 180° out of phase. These conditions can be met quite closely in the method described. However, Corbino (4) has shown that, on heating a metal filament by means of an alternating current, a second harmonic is introduced due to small variations in resistance with temperature in the course of current reversal. This effect could not be readily detected with an oscilloscope in the present investigation and was considered negligible as far as the qualitative course of the resistance vs. temperature curve of thorium is concerned. Temperature measurements were obtained by focusing a disappearing-filament type optical pyrometer onto a small hole drilled into the middle of the specimen.

X-ray diffraction data were obtained with a North American Philips Company high angle goniometer diffractometer which was adapted for high temperature investigations (5). A sketch of the goniometer specimen holder and furnace developed for this purpose is shown in Fig. 1. Both the base and furnace cover are water-cooled. The incident and diffracted x-rays pass through a 2.5-mil aluminum window which extends over a 180°C arc on the furnace cover. The furnace is evacuated through a

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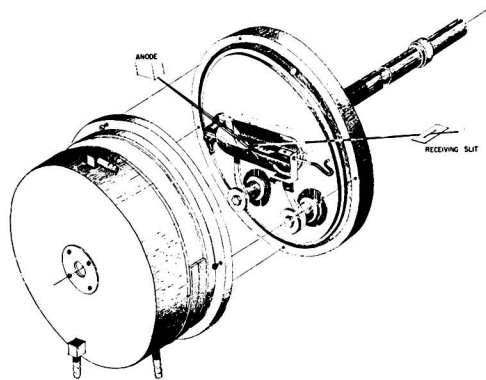


Fig. 1. Isometric projection of furnace and specimen holder attachment for x-ray diffraction goniometer.

hollow stainless steel shaft which extends through the goniometer.

Two types of specimens were used. One consisted of a thorium bar approximately $\frac{5}{16} \times \frac{3}{16} \times 3\frac{1}{2}$ in., held in place by the clamp shown on the left side of the furnace base in Fig. 1. The other consisted of a smaller piece of thorium, $\frac{1}{4} \times \frac{1}{8} \times \frac{3}{4}$ in., supported in an appropriate slot on a tantalum bar, the bar being held in place by the same clamp mentioned above. No appreciable reaction between the tantalum and the thorium was observed at temperatures up to 1575°C. The latter arrangement proved more satisfactory since thorium bars were found to sag when heated to this temperature.

Samples are heated by means of a tantalum sheet resistance element. Radiation shields surround the heating element to reduce radiation losses. The specimen is heated by radiation from the heating element and does not make direct contact with it. Temperature measurements are made by sighting an optical pyrometer on a small hole (No. 65 drill) drilled into the side of the specimen. The hole in the specimen is so arranged that it can be viewed through a glass window sealed onto the furnace cover and through a $\frac{1}{8}$ -in. hole drilled through the radiation shields.

EXPERIMENTAL RESULTS

The first evidence for a transformation in thorium was obtained from electrical resistance measurements. Results of measurements on a thorium specimen taken from cast metal are shown in Fig. 2. The resistance is seen to rise rapidly in the temperature range of 1425° to about 1525°C. The average heating rate through this temperature range was 1.6°/min. There is evidence of a second break in the curve at 1700°C which is believed to be due to incipient fusion; however, the bar did not melt in two until heated to 1740°C. Similar runs on other bars cut from cast metal, bars made from pressed

metal powder, and on Westinghouse metal, all gave a sharp increase in resistance at $1400^\circ \pm 25^\circ\text{C}$. The range of temperature over which this increase takes place is evidently related to the impurities in the metal and to some extent to temperature gradients in the specimen. Carbon is very effective in increasing the temperature at which the transformation begins. Metal containing as little as 0.2 wt % carbon along with the usual impurities no longer gives any definite indication of a transformation.

X-ray diffraction data confirmed the existence of a transformation in thorium. The metal transforms from face-centered cubic to body-centered cubic on heating to above 1400°C. Copper radiation and a nickel foil filter placed in the receiving slit were used in studying the transformation. In some cases where the alpha peaks were particularly strong, the corresponding beta peak was not completely suppressed. The scanning speed in each case was two degrees 2θ per minute. Fig. 3 shows the diffraction peaks of a sample which initially contained approximately 345 ppm carbon, 195 ppm nitrogen, 1000 ppm oxygen, and 1200 ppm metallic impurities. At 1375°C the 111 face-centered cubic peak was very strong. The temperature was then increased to 1415°C. The range from 26° to $33^\circ 2\theta$ was immediately scanned. As may be seen from this figure, a new peak identified as the 110 body-centered cubic peak appeared. This region was then rescanned and the diffraction peaks up to $146^\circ 2\theta$ recorded. The possible identification of the peaks is shown on the figure. The pressure in the system during the run was maintained between

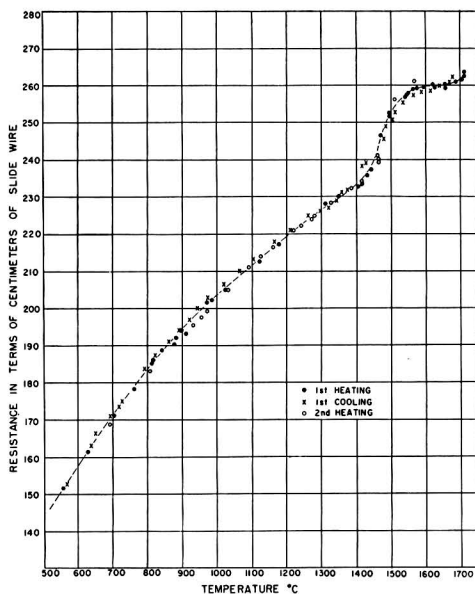


Fig. 2. Temperature dependence of the electrical resistance of thorium.

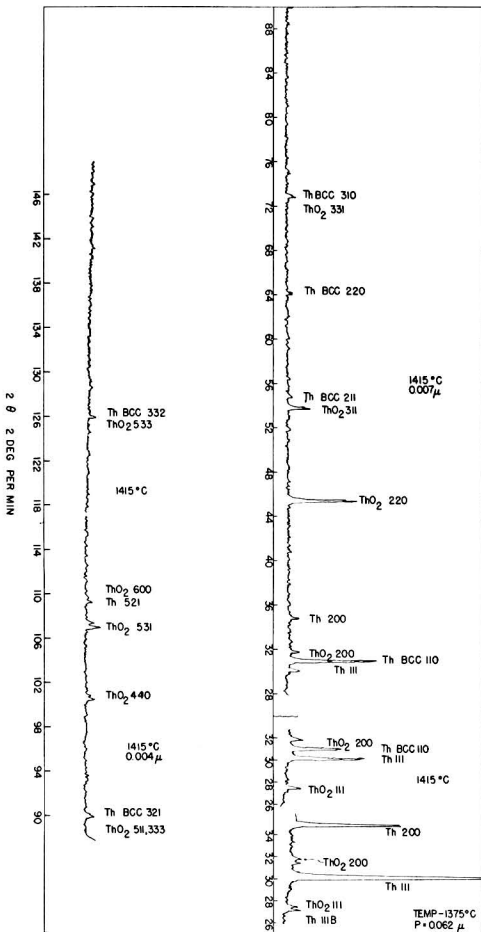


Fig. 3. Diffraction patterns of thorium contaminated with ThO_2 .

2.0×10^{-6} to 7.0×10^{-5} mm of Hg. The missing body-centered cubic peaks and the peculiar relative intensities of the peaks observed is believed to be due to excessively large grains and grain orientation.

Fig. 4 shows the nature of a thorium specimen surface after being heated for about six hours at temperatures between 1200° and 1500°C during the course of x-ray diffraction studies. The large dark spots are believed to be oxide particles in the metal initially. The fine structure is probably due to contamination by oxygen or other gaseous impurities during the heating operation. Large recrystallized grains and the outlines of the old grains are evident.

Fig. 5 shows the front reflection peaks obtained with a sample of iodide crystal bar thorium of unknown purity. At 1440°C only one face-centered cubic peak and two body-centered cubic peaks are present. At 1505°C only two body-centered cubic peaks remain; however, these two peaks are not the

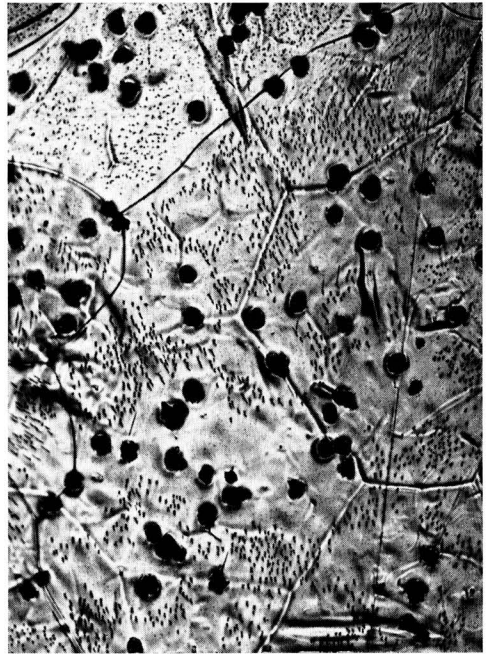


Fig. 4. Surface of thorium sample after about 6 hr at temperatures between 1200° and 1500°C , unetched. $100\times$.

same as the body-centered peaks present at 1440°C . A possible explanation for this observation is that a change in orientation of the grains results as the transformation goes to completion. Absence of thorium oxide peaks is noted.

Both tantalum and niobium lower the temperature at which the transformation begins to approximately 1375°C . The lowering of the transformation temperature may be due to solubility of these metals in body-centered thorium or due to removal of impurities which normally increase the stability of the face-centered modification. Tantalum, when added to thorium in small amounts, effectively removes carbon from solid solution to form insoluble Ta_2C . In this case the thorium matrix can be dissolved with nitric acid leaving the insoluble carbide as a residue. Niobium presumably does likewise. The extent of solid solubility of either niobium or tantalum in body-centered thorium is uncertain, but from atomic size considerations it is expected to be small. Zirconium, however, is very effective in lowering the temperature at which thorium transforms. Diffraction peaks obtained from a sample containing 1 wt % each of niobium and zirconium are shown in Fig. 6. It is evident from this figure that some of the body-centered phase is present at 1340°C and that the face-centered cubic phase has disappeared at 1375°C .

Small variations in alignment of the specimens along with the effects of orientation resulted in a

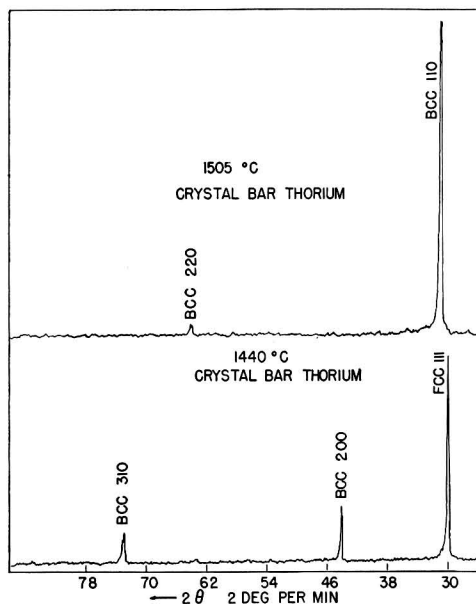


Fig. 5. Diffraction patterns of crystal bar thorium of unknown purity.

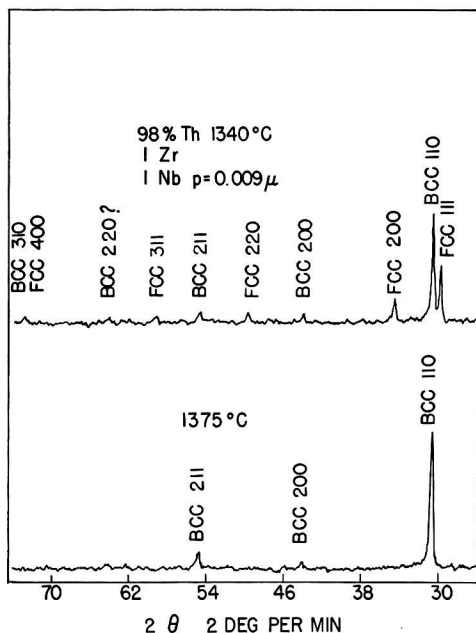


Fig. 6. Diffraction patterns of thorium containing 1 wt % each of niobium and zirconium taken at 1340° and 1375°C.

much greater variation in peak position than is normally obtained with well-aligned samples with small, randomly oriented grains. Nelson and Riley's (6) extrapolation method was used in determining the lattice constants. Individual peaks were also

scanned at one-fourth degree 2θ /min to obtain better resolution of the peaks. The uncertainty in the extrapolated value of the lattice constant of the body-centered thorium was found to be rather large due to the fact that the well defined peaks usually occurred only in the front reflection region and the total number of peaks was generally limited to five or less.

CONCLUSIONS

As a result of a large number of x-ray diffraction measurements on thorium metal containing approximately 345 ppm carbon, 195 ppm nitrogen, 1000 ppm oxygen, and 1200 ppm metallic impurities, it may be concluded that this metal transforms from face-centered cubic to body-centered cubic at $1400 \pm 25^\circ\text{C}$. The lattice constant of the body-centered metal at 1450°C is $4.11 \pm 0.01 \text{ \AA}$, and the extrapolated lattice constant of the face-centered cubic modification at the same temperature is $5.180 \pm 0.005 \text{ \AA}$. At room temperature the lattice constant of the metal used was $5.089 \pm 0.001 \text{ \AA}$.

Some contamination of the specimen surface by carbon on heating at 600° and 900°C was observed. This was probably because of outgassing of rubber vacuum seals or the Apiezon wax used to seal the aluminum window. Prolonged heating in this range usually resulted in the appearance of extraneous peaks which could be indexed as face-centered cubic thorium carbide. At temperatures above 1000°C , no difficulty in this respect was observed, possibly because of the rapid diffusion of carbon into the metal. Possible variation of the carbon content on the surface of the specimens due to these effects probably contributed to the observed variation in the lattice constants.

ACKNOWLEDGMENTS

The author wishes to acknowledge the cooperation and assistance of fellow members of the Ames Laboratory. The high temperature x-ray diffraction patterns were obtained with the assistance of Robert White.

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

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Anodic Behavior of Copper in HCl¹

LEE STEPHENSON² AND J. H. BARTLETT

Department of Physics, University of Illinois, Urbana, Illinois

ABSTRACT

Anodic behavior of copper in 2*N* HCl has been studied by both electrical and optical methods. The temporal behavior of current and voltage have been found, as well as the current vs. voltage characteristics. The anode surface has been observed both visually and photographically with the aid of conventional microscopes, and the anolyte has been photographed cinematographically using a schlieren microscope.

When the current is turned on, a layer, probably CuCl, starts to form at random nucleation spots on the anode. This grows until the whole anode is covered, at which time the current drops abruptly. Up until this time the anolyte becomes less concentrated, but the concentration may increase again after the current has become low.

The anode-calomel voltage may be written as $V = \epsilon(i) + ir$, where $\epsilon(i)$ becomes constant at high current densities. The values of $\epsilon(i)$ have been found by both the interruption and the direct method, and there appear to be at least four of physical significance. These values are -0.35 , -0.27 , -0.05 , and $+0.11$ v.

In general, the current drops twice before reaching its minimum value. If t_f is the time from the make to the first drop, and if $Q = \int_0^{t_f} i dt$, and if i_0 is the "initial" current after the make, then empirically $Q = 24(i_0 - 0.70)^{-0.63}$, where i_0 is in ma.

The anode layer is about 3μ thick in the steady state. When the circuit is broken, r and ϵ change rather rapidly (in about 0.1 sec), but the layer dissolves off slowly.

INTRODUCTION

In an endeavor to further the understanding of electrochemical phenomena, such as overshoot and oscillations, which occur in biological systems, Bartlett (1) studied the anodic behavior of iron in aqueous H₂SO₄ with special attention to various kinds of transient phenomena which may arise when the applied voltage is changed. The work was continued by Bartlett and Stephenson (2) with emphasis now on the steady-state behavior of passive and active iron, and on the transients resulting from brief interruptions of the active steady state. Microscopic observation of the anode *in situ* revealed that evolution of hydrogen caused disruption of the layer which tended to form, so that this introduced an uncontrollable variation with resulting lack of reproducibility. The conclusion was reached that the Fe | H₂SO₄ system is an undesirable one to use for the study of layer formation, which seems to be basic for any analysis of overshoot and oscillation.

Fortunately, other systems do exhibit these transient phenomena, and these are much more reproducible.³ Bartlett and Stephenson decided to

investigate the system consisting of a copper anode in aqueous HCl. This is admirably suited for the study of layer formation because of the following properties: (a) Cu is attacked only very slowly by 2*N* HCl; (b) the anode layer which is formed is readily detected by simple optical means; (c) rates of reaction are such that the transient phenomena can be followed easily; (d) compositions of the layer and the soluble anode product are known; and (e) no undesirable products are formed during electrolysis. The purpose of the present paper is to report on various physical changes which take place at the surface of a copper anode immersed in HCl, and on changes occurring in the diffusion layer next to this anode. The work may be regarded as a theoretical contribution to the behavior of metal electrodes covered with precipitated salt, as found in corrosion reactions.

Procedure

The experiments to be described fall into two main categories: electrical and optical. The electrical experiments involve studies of temporal behavior of current and voltage, and of the current vs. voltage characteristics. The optical experiments consist of both visual and cinematographic observation of the anode surface with conventional microscopes, and of cinematographic studies of the

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² Present address: California Research Corporation, La Habra, California.

³ The high degree of reproducibility in the system re-

ported on here is evident from Fig. 5-8, 13, and 14, where each point represents one run only and is not an average of several runs.

analyte using a schlieren microscope. The optical experiments are carried out in conjunction with the electrical experiments so that accurate correlation of all related phenomena is possible.

Apparatus

Cell.—The circuit employed in these experiments is shown semipictorially in Fig. 1. The electrolytic cell consisted of a rectangular box made of glass with an optical window of glass 0.1 mm thick in one face to permit microscopic observation of the anode *in situ*. The inside dimensions of the cell were 2.5 x 7.5 x 7.5 cm. The cell contained 110 ml of an aqueous solution of hydrochloric acid, into which were placed two working electrodes and a reference electrode. Unless otherwise noted, the acid concentration was 2 moles/l (2*N*) and the temperature was 25°C. Preliminary experiments were carried out in both air-saturated and oxygen-free solutions in order to determine the effects of dissolved oxygen on the phenomena to be observed. No differences in the transient behavior were apparent, and microscopic observations failed to show any changes in the anode film due to dissolved oxygen. Consequently, the more convenient air-saturated solutions were used. Because of physical limitations imposed upon the structure and the orientation of the anode by the microscopic experiments and the schlieren experiments, it was decided to conduct all experiments with a vertical anode and to permit free convection of the analyte. The anode structure consisted of a vertical brass rod with a 1 cm length of #14 (1.63 mm diameter) copper wire (Anaconda) soldered horizontally into its lower end. Picein 105⁴ covered the entire assembly except for the end cross section, A, of the copper wire, which constituted the anode surface. Filed anodes were prepared using a Nicholson "Mill Smooth" file. Electropolished anodes were prepared by mechanical polishing down to 4/0 polishing paper (Norton) followed by electropolishing in 50% orthophosphoric acid. The cathode, K, was a 0.005 in. thick platinized platinum sheet, 3.0 x 3.3 cm, supported by a brass rod which was covered with Picein. A 0.1*N* calomel half-cell was used as the reference electrode. Provided the distance between the anode and the cell walls was at least 2 mm, the transient behavior was found to be independent of cell geometry (2).

The potential measurement, source of emf, recording of current and voltage, and interruption techniques were as described in a previous paper (2). In addition, a Brown recording potentiometer (0–10 mv) was used to record slow transients (i.e., those lasting longer than about 20 sec). The external

⁴ Obtained from E. H. Sargent Company, Chicago, Illinois.

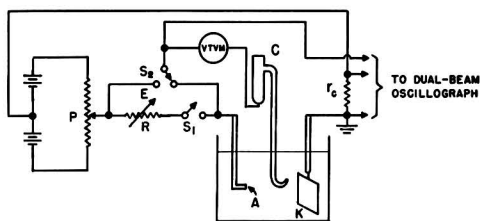


Fig. 1. Basic circuit. P, potential divider; R, 200 ohm helipot; VTVM, vacuum tube voltmeter; A, 0.021 cm² copper anode; C, 0.1*N* calomel reference electrode; K, 10 cm² platinized cathode; r_c, current resistor.

circuit resistance was controlled by a 200 ohm helipot, R.

Microscope and accessories.—For visual observation of the anode surface, a microscope was provided with a special mechanical stage to hold the electrolytic cell, electrodes, etc. For most work, a 16 mm (10×) objective having a numerical aperture of 0.25 and a working distance of 6 mm was used, together with a 10× eyepiece. The anode was illuminated obliquely to obtain maximum contrast. A 35 mm Praktica FX single-lens reflex camera was used to obtain photomicrographs.

Cinematographic microscope.—Cinematography of the anode surface was accomplished with a conventional 8 mm home movie camera, Bell and Howell Model 134-V. The camera lens, an f/1.9 Super Comat, was removed from the camera and mounted backward (in order to preserve the conjugate relationship for which the lens was corrected) on a short extension tube. This arrangement provided an excellent cinematographic microscope having a primary magnification of 3.4 diameters. An auxiliary lens and 45° prism were mounted in the side of the extension tube to permit simultaneous recording of the current and voltage

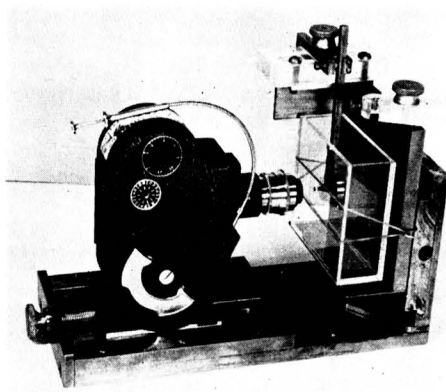


Fig. 2. Cinematographic microscope

deflections on the oscillograph screen. Fig. 2 shows the principal features of this apparatus.

Schlieren photography.—Information about the diffusion layer was obtained by using a specially constructed schlieren microscope (3). This is an optical instrument in which the intensity of light incident on the photographic film at a certain point is a linear function of the gradient of the index of refraction at the corresponding point in the object space. Even though this method has not yet been made quantitative at concentration gradients as high as those occurring in the present work, it still is very helpful in furnishing a general picture of what is occurring. Schlieren motion pictures of the diffusion layer were taken with the aid of the 8 mm camera used for microphotography.

MAKE TRANSIENTS

General nature of transients.—If a freshly filed anode is placed in the solution and the circuit is then closed, the nature of the ensuing current vs. time curve (here designated as a “make transient”) will depend on the external emf E and the external resistance R (1).

The complete circuit will be considered as consisting of two parts, the internal part and the external part. The internal part is defined as that part which extends in the cell from the anode metal to the tip of the calomel electrode. Its resistance will be denoted by r . The external part of the circuit is that part which metallicly connects the anode to the cathode, plus the part from the cathode to the calomel electrode tip. Its resistance will be termed R . If i is the total cell current measured in the external circuit, the anode-calomel voltage V is given by

$$V = E - iR \quad (1)$$

If E and R are held constant, i can still vary, but V will also vary. In the i - V plane, the above equation will be represented by a straight line, which will be called the load line, in analogy to vacuum tube terminology. (The resistance R consists mainly of the resistance of the helipot, and we shall regard as negligible the resistance of the leads, of the potential divider circuit, and of the solution between cathode and calomel, because these total approximately 1.5 ohms, or only 1% of the minimum resistance employed in the present work.)

A typical make transient for medium R (140 ohms) and high final voltage V is shown in Fig. 3a. At the very beginning, there is a spike (not shown) lasting about 10^{-5} or 10^{-4} sec. The current then falls rapidly from the “initial” value i_0 and becomes approximately independent of time. This region will be called the first plateau. The current actually goes

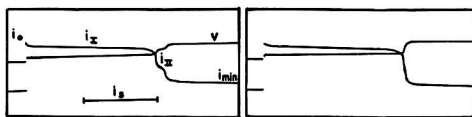


FIG. 3. Make transients. $E = +0.50$ v, $R = 140$ ohms. a, Left, freshly filed anode; b, right, electropolished anode.

through an inflection point, i_1 , decreasing more or less slowly. After a rather abrupt drop to a second plateau (current i_{11}), the current drops again, then varies slowly. For the case shown in the figure, it goes through a minimum i_{min} and then rises to the steady state value i_{∞} . If, however, i_0 is sufficiently high, such a minimum is not observed and the current will fall continually until i_{∞} is reached. The current may overshoot one or more times before settling down to the steady value, 1.7 ma. This is illustrated in the semilogarithmic plot of Fig. 4.

Electrode potential and resistance.—If an appreciable current flows, the anode-calomel voltage will, in general, differ from the reversible value, V_{rev} . The overvoltage is defined as the difference between the observed voltage (at a given current) and the reversible value. It is regarded as composed of three distinct contributions: resistance overvoltage $V_r = ir$, concentration overvoltage or polarization V_c , and “activation” overvoltage V_a (4).

The anode-calomel voltage may then be written as

$$V = V_{rev} + V_a + V_c + V_r = \epsilon + ir. \quad (II)$$

The quantity $\epsilon = V_{rev} + V_a + V_c$ will be termed the electrode potential for present purposes. If this is constant for a certain set of circumstances, the locus of i vs. V will be a straight line with intercept ϵ and slope $1/r$. This determination is called the direct method (5) of obtaining ϵ and r . Another

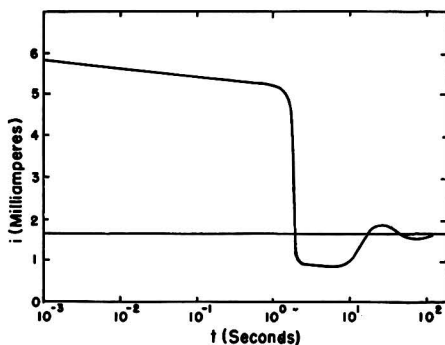


FIG. 4. Make transient for freshly filed anode. The horizontal line at 1.7 ma represents the steady-state current. $E = +0.50$ v, $R = 140$ ohms.

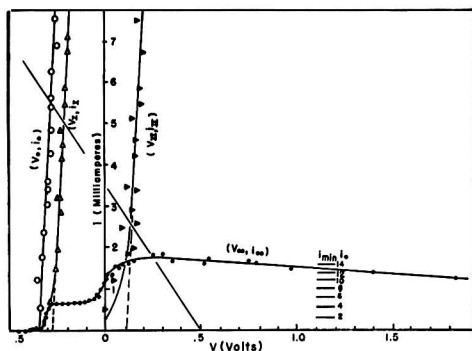


FIG. 5. Characteristic curves for the Cu | HCl (2N) system at 25°C with a freshly filed anode having an area of 2.1 mm².

method which may be used to check or complement this is the interruption method. This consists in breaking the circuit and observing V before and after, as well as i before, the break. Then $\epsilon = V_{\text{off}}$ and $r = (V_{\text{on}} - V_{\text{off}})/i$. Both methods were used, and they agree in all cases where they are applicable. The interruption method will not be suitable if the recording apparatus is not sufficiently fast, for a rapid decay of ϵ may escape detection. Even where this decay is observed, one must extrapolate back to $t = 0$ in order to find the value of ϵ at the time of the break. The results of Hickling and Salt (6), based on extrapolation, were criticized adversely by Frumkin (7).

For high current densities, the value of ϵ is constant in the steady state (8) and at certain critical points (for the system Cu | HCl), as will now be shown. These critical points occur when i is equal to i_0 , i_I , and i_{II} , respectively. As may be seen from Fig. 5, the loci (V_0, i_0) , (V_I, i_I) , and (V_{II}, i_{II}) , which shall be called "characteristics", become straight, mutually parallel lines above approximately 1 ma. (Similar behavior has been found for the steady state, for Hickling (8) stated that "there is a fairly general tendency for the overvoltage to approach a constant maximum value" at high current densities.) The reciprocal of the common slope of the characteristics equals the resistance, and is 12 ohms for the system (Cu | 2M HCl). Thus, the cell's internal resistance does not change appreciably until after the second plateau has been reached.

The values of ϵ determined by this direct method are $\epsilon_0 = -0.35$ v, $\epsilon_I = -0.27$ v, and $\epsilon_{II} = +0.11$ v. In other words, at high current densities these experiments show that the overvoltage (excluding that due to ohmic resistance) has one constant value for i_0 , another for i_I , and another for i_{II} .

Two of the above values of ϵ were confirmed by

interruption experiments, which resulted in $\epsilon_0 = -0.35$ v and $\epsilon_I = -0.27$ v. However, when the current during the second plateau and later is interrupted, the value of V after 10^{-4} sec is $\epsilon_{II} = -0.05$ v. This is reconcilable with the result of the direct method if it can be assumed that there is a rapid decay ($<10^{-4}$ sec) from $\epsilon_{II} = +0.11$ v to $\epsilon'_{II} = -0.05$ v. (The recording apparatus used in the present experiments was relatively slow, being incapable of detecting decay constants appreciably smaller than 10^{-4} sec.) The value of $\epsilon = 0.11$ v does seem to have physical significance (cf. "Break Transients").

Typical curves showing the variation of ϵ and r with time as determined by the interruption method are given in Fig. 6. Data were obtained for freshly filed anodes with $E = +0.20$ v and $R = 140$ ohms, and are plotted on the assumption that the entire voltage change at the break is due to an ir drop.

On open circuit, the potential of the copper electrode is $\epsilon_{00} = -0.44$ v (with respect to 0.1N calomel). Immediately after the circuit is closed, the potential jumps to $\epsilon_0 = -0.35$ v, as is evidenced by a small dot on the film. (The switch contact S_1 [Fig. 1] bounced for about 10^{-3} sec after closing, and thus provided sufficient break to observe this value of ϵ .) The potential then rises less rapidly to $\epsilon_I = -0.27$ v. It stays at this value until the end of the first plateau, when it changes abruptly to

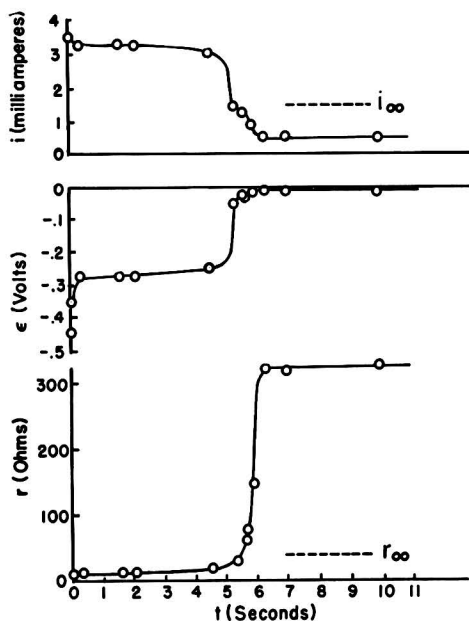


FIG. 6. Temporal behavior of ϵ and r following make. $E = +0.20$ v, $R = 140$ ohms.

$\epsilon'_{11} = -0.05$ v, the potential of the second plateau, where it remains for the rest of the transient.

The resistance r remains essentially constant at its initial value, $r_0 = 12$ ohms, until the end of the first plateau. Then, soon after the ϵ jump, it increases abruptly to a maximum value and decreases slowly toward its steady-state value r_{∞} , ϵ staying practically constant⁵ at -0.05 v.

If one now re-examines the i vs. t curve with an eye to stating on what portions ϵ varies and on what portions r varies, the following conclusions are reached:

1. The drop in current from i_0 to i_1 and the drop from i_1 to i_{11} are due primarily to changes in ϵ , while the drop from i_{11} to i_{\min} is due primarily to a change in r . In the case of electropolished anodes where the transition from i_1 to i_{\min} is relatively smooth, it is presumed that the changes in ϵ and r occur almost simultaneously.

2. Variations of the cell current subsequent to the current drop are due primarily to changes in r , for ϵ remains approximately constant at $\epsilon_{11} = 0.11$ v.

Durations of plateaus.—The duration of the first plateau is found to depend on i_0 . Let t_1 be the time from the make to the inflection point at the drop from i_1 to i_{11} , and let $Q = \int_0^{t_1} i dt$. Then empirically,

$$Q \approx i_1 t_1 = 24 (i_0 - 0.70)^{-0.53} \quad (\text{III})$$

(This is shown in Fig. 7.) If E and R be given, then i_0 and i_1 can be found from the intersection of the load line with the characteristics. Then, from equation (III), t_1 can be estimated. It will decrease as i_0 increases. The value 0.70 in equation (III) corresponds to the steady-state current on the lower plateau (see below).

The duration of the second plateau appears to be affected by the condition of the anode surface, being a maximum for a filed surface and a minimum for an electropolished surface. Indeed, with an electropolished anode the second plateau is sometimes entirely absent, its expected location being marked only by a slight discontinuity in the slope of the i vs. t curve (Fig. 3b).

Prediction of general features of a make transient.—Once the "characteristics", i.e., the straight lines associated with the critical points, have been found, it is an easy matter, knowing equation (III), to give the main features of a transient corresponding to any values of E and R .

⁵ Under similar circumstances, the potential drop across the diffusion layer has been deduced to be negligible. See reference (9).

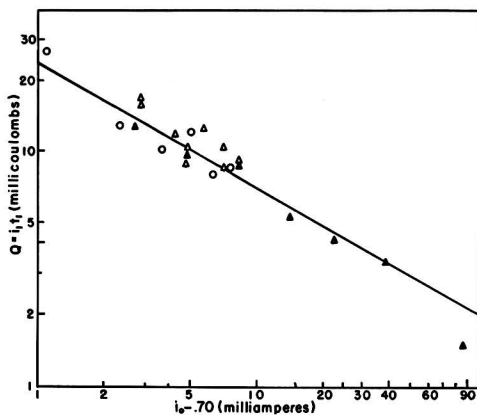


FIG. 7. Q as a function of i_0 for both freshly filed and electropolished anodes. $Q = 24 (i_0 - 0.70)^{-0.53}$

If equations (I) and (II) are solved for i , the result is

$$i = \frac{E - \epsilon}{R + r} \quad (\text{IV})$$

One can substitute in the values of E and R , set $r = 12$ (the value of the solution resistance), and the values ϵ_0 and ϵ_1 , to obtain i_0 and i_1 . Alternatively, these can be found graphically by letting the load line intersect the characteristics corresponding to ϵ_0 and ϵ_1 , respectively. The values of V are dependent on those of i by equation (I).

Once i_0 and i_1 are known, t_1 can be obtained from equation (III), so that the main features of the make transient up to the time that the current first drops can be given beforehand. Thus it is seen that the characteristic lines, which may be obtained quite easily, are extremely useful in prediction.

The current minimum.—In many cases the current passes through a minimum shortly after the final current drop. For currents up to 15 ma, i_{\min} is found to depend mainly upon i_0 , as illustrated in Fig. 8. There is also a dependence of i_{\min} on the condition of the anode surface, it being smaller for electropolished anodes than for ground anodes.

Schlieren study of the anolyte.—The qualitative nature of changes occurring in the diffusion layer at the anode was determined with a schlieren microscope. The pictures shown in Fig. 9 were taken using a freshly filed anode, with $E = 0.50$ v and $R = 140$ ohms. The schlieren knife edge was adjusted to show positive and negative gradients with equal clarity, and so oriented with respect to the anode (which appears in silhouetted profile at the left of the photographs) that bright regions corresponded to a refractive index (and concentration) which was increasing toward the anode, and

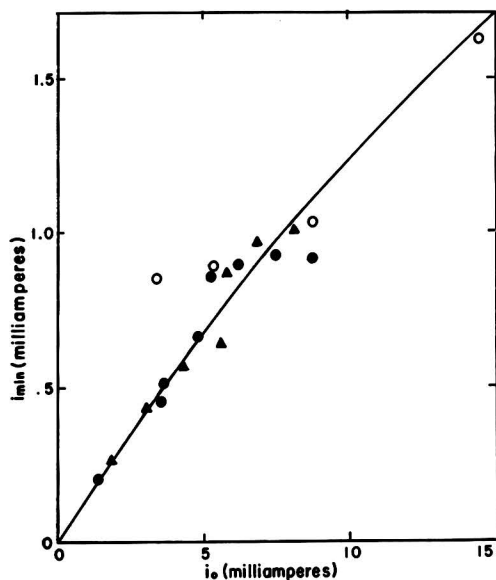


FIG. 8. Minimum current vs. initial current for a freshly filed anode.

dark regions corresponded to a refractive index (and concentration) which was decreasing toward the anode.

At $t = 0$, immediately before closing the switch, the anolyte is seen to have a uniform concentration throughout the region in which the diffusion layer is expected to develop. The bright line outlining the face of the anode is due primarily to diffraction (10), but may be enhanced somewhat by the presence of products from the acid's slow attack on the anode. After electrolysis has proceeded for 0.7 sec, a dark region is observed extending out from the anode into the solution approximately 0.15 mm (measured at the center of the anode). Since the refractive index is decreasing toward the anode in this region, it can only be a region in which the HCl concentration is decreasing toward the anode; i.e., Cl^- is being consumed at the anode-solution interface. (Some of the photographs show a brightening of the anolyte nearest the anode which lasts for about one-third the duration of the first plateau. This is as yet not explained, and is not relevant to the present discussion.) At 1.3 sec and 2.0 sec the HCl-depleted region has advanced to approximately 0.27 mm and 0.33 mm, respectively. Comparing the photographs taken at 2.0 sec (near the end of the first plateau), at 2.1 sec (on the second plateau), and at 2.2 sec (near the current minimum), it is seen that no change whatever occurs in the diffusion layer when the current drops. After 4 sec have elapsed, the HCl-depleted region has nearly reached its maximum extent of about 0.48 mm, the reduced

density of this region being evidenced by the fact that it is carried upward by convection. At the same time it is observed that a bright region, corresponding to a refractive index which increases as the anode is approached, has begun to form at the face of the anode. At 6 sec the current has reached its minimum (Fig. 4), the HCl-depleted region has advanced to its maximum extent, and the material of the bright region of the anode product has begun to stream from the bottom of the anode, showing that its density is greater than that of 2N HCl. After 10 sec have elapsed, the current has begun to rise toward its steady-state value, the HCl-depleted layer has begun to recede, and the anode product has established a steady downward flow which tends to counteract the upward convection previously established by the HCl-depleted layer. At 300 sec the current has reached its steady-state value. The HCl-depleted region is not only appreciably reduced in extent, but is now being swept downward by the anode product.

The anode reactions.—Since, when current flows, Cl^- disappears from solution and Cl_2 is not observed to be liberated, the Cl^- must be consumed by some reaction involving the oxidation of copper. The resulting products are at least two in number, for it is observed that a layer forms on the anode and a viscous stream pours down from it after the layer has been completed.

Some evidence as to the nature of the anode reactions is furnished by the existence of the two

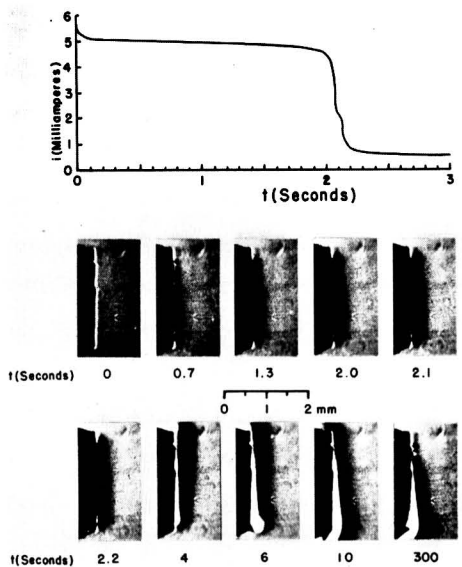
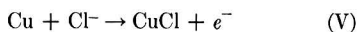


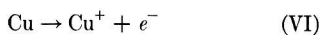
FIG. 9. Schlieren study of the anolyte following make. $E = +0.50$, $R = 140$ ohms.

electrode potentials, $\epsilon_I = -0.27$ v and $\epsilon'_{II} = -0.05$ v. The former is observed when at least part of the anode surface is exposed to the solution, while the latter potential corresponds to the surface being completely covered with the above-mentioned layer. As will be seen below, ϵ_I differs from ϵ_0 because of concentration polarization. The potential ϵ_0 is characteristic of the anode before much layer has had time to form. The anode potential ϵ_I is practically constant until the sudden transition to ϵ'_{II} , or in other words is almost uninfluenced by the layer formation until the layer is about complete.

It is necessary, then, to postulate one type of reaction for the bare surface and another for the covered surface. According to Gatty and Spooner (11), "At the moment of immersion of a Cu electrode in aqueous aerated solution, the electrode is covered with a film of Cu_2O . In concentrated acid chloride solutions, (this) film is readily broken up, (and) the electrode potential will be close to that of the anodic field of bare metal. The electrode tends to establish the $\text{Cu} | \text{CuCl} | \text{Cl}^-$ electrode potential, CuCl being the least soluble of the copper chlorides. Complex ion formation takes place between the anodically formed CuCl and the halide in solution." The picture which the authors have developed, and which is consistent with all the known facts, is as follows: (A) the initial reaction is between chloride ions in solution and copper metal, resulting in the formation of CuCl layer on the anode; the potential ϵ_I is then associated with the reaction



(B) when the surface is covered, this reaction is supplanted by another, to which the potential ϵ'_{II} corresponds. According to Wagner (12) "depletion of chloride ions will yield a rather well-defined electrode potential corresponding to a copper electrode in a solution saturated with CuCl in the absence of excess electrolyte, especially HCl ." This reaction may be



Cuprous ions can diffuse through the CuCl layer until they meet with chloride ions, and then one may have the reaction



Also, CuCl is known to react with excess Cl^- to form the soluble, colorless complexes CuCl_2^- and CuCl_3^{2-} (13-16). It is assumed that the removal reaction is



Layer thickness.—If the anode reaction is as deduced above, then a knowledge of Q affords a

convenient means for estimating the thickness of the anode layer at the time the current drops. Assuming that Faraday's laws apply, Q/zF is the number of moles of CuCl formed up to that time. Assuming further that a negligible amount of CuCl is dissolved before the current drops, the thickness of the layer is given by $\delta = QM/zFd$, where M is the gram-molecular weight of CuCl , $zF = 96,500$ coulombs/mole, A is the anode area, and d is the density of CuCl . Taking, for example, the value $Q = 10.5$ millicoulombs (for $i_0 = 5.6$ ma) it is found that $\delta = 1.5 \times 10^{-4}$ cm. (Clearly, the CuCl layer cannot be expected to appear in the photos of Fig. 9, for its thickness is far beyond the limit of resolution of the schlieren microscope.)

It is also possible to estimate the thickness of the layer in the steady state by breaking the circuit and observing how long it takes for the layer to be removed completely. The rate of removal after interruption is assumed to be the same as the rate of formation in the steady state, namely i_∞/zF moles/sec. The thickness of the steady-state layer will therefore be given by $\delta = i_\infty M t / zF A d$, t is the time required for removal. With the aid of a microscope equipped with circularly polarizing film to improve image contrast, visual observation of the anode revealed that the time required for complete removal of the layer depends upon the value of V_∞ at the time of interruption, typical values of t and δ calculated from them being as follows:

V_∞ (v)	t (sec)	δ (μ)
+0.20	9.6(± 0.8)	2.3(± 0.2)
+0.80	14.9(± 1.0)	3.3(± 0.2)
+1.40	18.0(± 1.6)	3.5(± 0.3)

These values for δ indicate that the steady-state layer thickness is probably of the same order of magnitude as that found when the current drops from i_I to i_{\min} .

Layer growth.—Moving pictures of the anode surface taken at 64 frames/sec show that the layer begins to form at many randomly distributed points as soon as electrolysis begins, and that the growth from these nuclei takes place in a sideways manner. The current drops immediately after the pores of the nearly completed layer have been so reduced in size that they are no longer resolvable on the film (i.e., diameters reduced to roughly 5μ or less). Fig. 10 shows a series of photomicrographs of the anode face taken during the initial transient when $E = +0.70$ v and $R = 140$ ohms. Fig. 10(a) shows the electropolished anode immediately before electrolysis begins. Because of the oblique illumination employed, a truly specular surface would be completely dark. The bright spots which are observed are due to tiny pits left by electropolishing

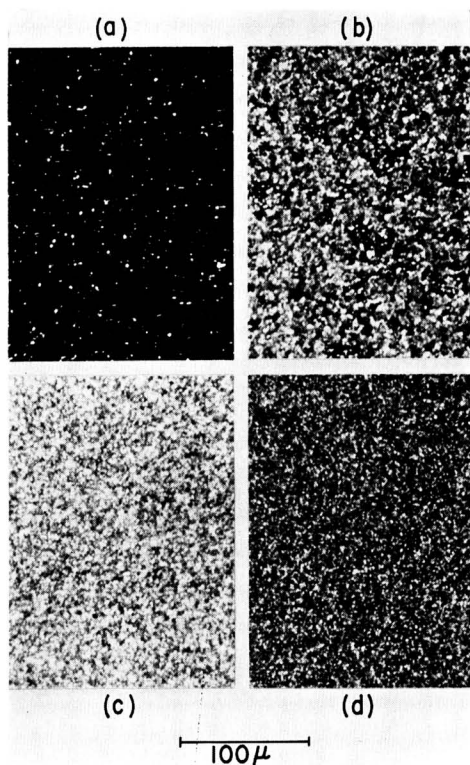


FIG. 10. Photomicrographs of the anode. (a) Before electrolysis; (b) midway on the first plateau; (c) at current minimum; and (d) steady state. $E = +0.70$ v; $R = 140$ ohms.

(17) and to a slight amount of etching which takes place while the microscope is being focused upon the immersed electrode.⁶ Fig. 10(b), taken approximately midway on the first plateau, shows that the free surface (dark areas) is greatly reduced by the sideways growth of the layer although no appreciable change in the cell current has occurred up to this time. Approximately 5 sec after the current drops, it reaches a minimum. At this point, the completed layer appears as in Fig. 10(c). The current then rises until the steady state is reached (after about 5 min of electrolysis) and then the layer appears as shown in Fig. 10(d).

BREAK TRANSIENTS

Dependence of potential decay on steady-state voltage.—Events subsequent to current interruption yield information on the layer removal process

⁶ It was found that the undesired etching could be inhibited by making the electrode cathodic while the necessary optical adjustments were being made (cathodic current density approximately 1 ma/cm²). However, this method was not employed.

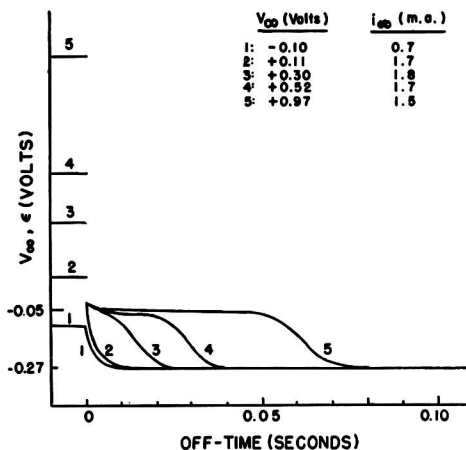


FIG. 11. Potential decay following interruption of the steady-state current, shown for various steady-state conditions.

alone, thus enabling one to separate this from that of layer formation. The curves in Fig. 11 show how the potential V varies after the break has been made, for different initial steady-state voltages V_{∞} . For values of V_{∞} greater than approximately 0 v, ϵ drops quickly to -0.05 v,⁷ remains approximately constant for a brief time depending on V_{∞} , and then drops suddenly to $\epsilon_1 = -0.27$ v. The potential vs. time curve has the same shape for passive iron (Fig. 12) in H_2SO_4 as it does for copper in HCl, which may indicate that similar mechanisms are operative in the two cases. The make curve for the transition from active iron to passive iron has been interpreted in terms of the formation of a layer, and now it is seen that the break curve for the passive-active transition resembles the break curve in copper, where it is known that there is a layer present. The evidence for a layer on passive iron is thus made stronger than ever, and it now remains to identify positively the reactions by which it is formed and removed.

In copper, for $V_{\infty} < -0.05$ v, the potential decay is somewhat like an exponential from V_{∞} to ϵ_1 . From ϵ_1 on, the potential falls slowly to $\epsilon_0 = -0.44$ v, this process lasting many minutes (see Fig. 13). Although this method of recording does not indicate that anything special occurs at $\epsilon_0 = -0.35$ v, still one observes that stirring right after interruption does reduce the potential immediately to this value

⁷ It has already been supposed that this is really composed of two drops, with $\epsilon_{11} = 0.11$ v as the intermediate value. The value -0.05 v is presumably the true electrode potential (i.e., without overvoltage) of the completed layer. The value $\epsilon_1 = -0.27$ v agrees with the potential of Cu in 2N HCl saturated with CuCl (R. S. COOPER, private communication).

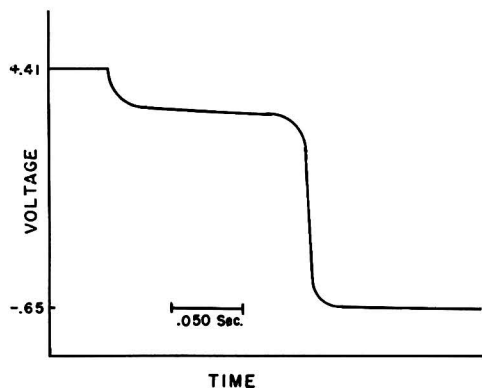
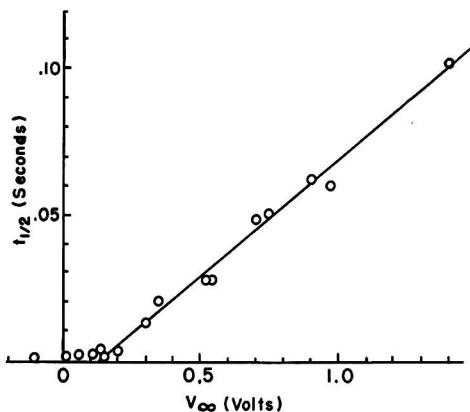


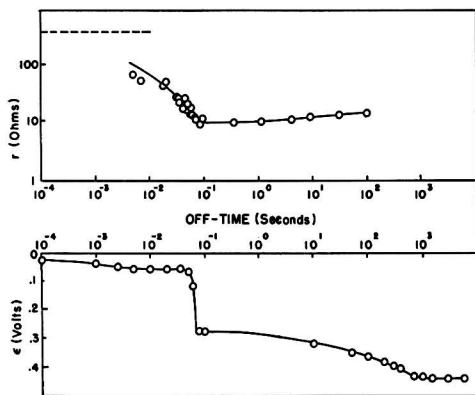
FIG. 12. Break transient for passive iron

FIG. 14. $t_{1/2}$ vs. V_{∞}

of -0.35 v. This suggests that the difference between ϵ_0 and ϵ_1 is due to concentration polarization.

The duration of the break plateau ($\epsilon = -0.05$ v) depends linearly upon V_{∞} . (The duration is defined arbitrarily as the time from the interruption until the midpoint $\epsilon = -0.16$ v is reached, and will be denoted by $t_{1/2}$.) Fig. 14 is a plot of the duration $t_{1/2}$ against V_{∞} . It is a straight line which has an intercept of $+0.11$ v on the V -axis. This is regarded as evidence that $\epsilon = +0.11$ v is the potential of the completed layer, as is also found from the characteristic curves. Below $+0.11$ v, the layer is not complete, so that there is no preparatory time necessary to make part of the surface bare.

Temporal behavior of ϵ and r .—Fig. 13 shows the temporal behavior of ϵ and r following interruption of an arbitrarily chosen steady-state condition, $V_{\infty} = +0.75$ v and $i_{\infty} = 1.6$ ma. To obtain these data, the steady-state current was interrupted for a predetermined length of time, at the end of which

FIG. 13. Temporal behavior of ϵ and r following interruption of the steady state. $V_{\infty} = +0.75$, $i_{\infty} = 1.6$ ma.

the circuit was closed again. The electrode potential, ϵ , was taken to be the value of V immediately before the circuit was closed, since equation (II) becomes $V = \epsilon$ when the current is interrupted. The resistance r is determined by measuring $V_{on} = \epsilon + ir$ just before the circuit is broken, or just after it is made, and also measuring $V_{off} = \epsilon$ just after the circuit is broken, or just before it is made. Eliminating ϵ and solving for r it is seen that in either case

$$r = (V_{on} - V_{off})/i \quad (\text{VIII})$$

With the apparatus at hand it was not possible to obtain off-times shorter than 0.005 sec. The dashed line at $r = 400$ ohms represents the value of r at the instant of interruption (calculated on the basis that $\epsilon = \epsilon_{11} = +0.11$ v).

The data show that the abrupt drop in ϵ does not begin until the decay of r is more than 96% complete.

Schlieren study after break.—When the steady-state current is interrupted, fairly rapid changes in the anolyte seem to occur, but whether or not they correspond to the sudden drop in ϵ cannot as yet be stated with certainty. The schlieren photographs in Fig. 15 show that 10 sec after interruption the Cl^- gradient is nearly erased, while the stream of anode product continues almost unabated as the layer continues to dissolve. After 20 sec the Cl^- gradient can no longer be detected and the CuCl_2^- gradient has begun to iron out, all of the layer having been removed at this time. After 40 sec the CuCl_2^- is no longer streaming from the anode, and by the time 60 sec have elapsed the anolyte has almost regained the composition of the main body of solution. From Fig. 13 it can be seen that the time required for erasure of the concentration gradients is about the same as the time required for decay from $\epsilon_1 = -0.27$ v to $\epsilon_0 = -0.35$ v. This is consistent with

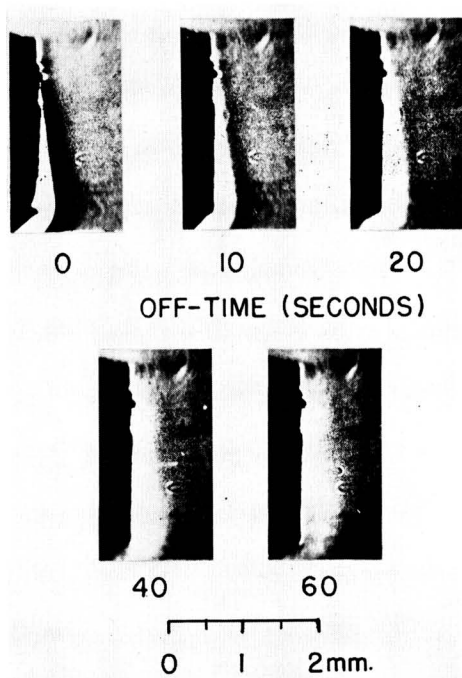


Fig. 15. Schlieren study of the anolyte following interruption of the steady state. $V_{\infty} = +0.25$ v, $i_{\infty} = 1.8$ ma.

the previous hypothesis that the difference in these two potentials is to be attributed to concentration polarization.

DISCUSSION

The present work has demonstrated the nature of the processes associated with that portion of the make transient up to the current minimum. The early layer growth starts from randomly distributed nuclei on the anode surface and proceeds radially so that little knobs are formed. When these have grown sufficiently, they touch each other. The anode will then have a thin continuous layer upon it, and this needs (18) to be only a few molecules thick (i.e., of the order of 10^{-7} cm) in order to establish the potential characteristic of a copper electrode covered with CuCl. It was found (Fig. 8) that ϵ may increase suddenly without a corresponding change in r , indicating that the portion of the layer responsible for the increase must have negligible resistance and, consequently, be very thin. The subsequent increase in r indicates the completion of a relatively thick layer, because it exhibits a large resistance. It should be emphasized that no sharp distinction or boundary is imagined to exist between the thin ϵ -layer and the thick r -layer. Both are

imagined to grow simultaneously during the course of a transient and to be completed at very nearly the same time, completion of the r -layer usually lagging, but never preceding that of the ϵ -layer.

A kinetic explanation will be achieved when one can predict quantitatively how the electrode potential ϵ and the resistance r will vary with time. At the end of the first plateau, ϵ changes rapidly, and this may indicate the rate at which the surface becomes covered (3). From the beginning of the second plateau, however, ϵ is nearly constant, so that the current changes are due to changes in the resistance r . The detailed mechanism of how these changes occur is still obscure, but it may be possible to learn more about it by suitable make and break experiments. In particular, data are needed for the variation of r with time when the steady state is interrupted for times less than 0.01 sec.

SUMMARY

When the circuit is closed in the Cu | 2N HCl(aq) | H₂(Pt) system, the current exhibits a very brief initial spike. The anode-calomel potential may be represented at all times $>10^{-5}$ sec by $V = \epsilon + ir$, where ϵ , the electrode potential, has no noticeable dependence on i at high currents, and r , the resistance within the cell between anode and calomel, is ohmic in nature. The open circuit voltage is -0.44 v, and has four characteristic values thereafter. Immediately after the spike, $\epsilon = \epsilon_0 = -0.35$ v. The current drops from i_0 to an approximately constant value i_1 (first plateau), and ϵ becomes $\epsilon_1 = -0.27$ v. (This change is attributed to concentration polarization.) The charge Q which must flow before the current completes its drop to a new constant value i_{11} (second plateau) is connected with i_0 by the empirical relation $Q = 24(i_0 - 0.70)^{-0.53}$. The value of ϵ_{11} as determined by extrapolation of the (V_{11}, i_{11}) plot is $\epsilon_{11} = +0.11$ v; the value found from interruption experiments is $\epsilon'_{11} = -0.05$ v. This could be accounted for by an overvoltage term with a decay time of 10^{-5} sec or less. The value of r is constant up to the second plateau, and corresponds to the resistance of the solution. The second plateau has a duration which is shorter, the smoother the surface. It is followed by a rapid drop in i and the associated rapid increase in resistance. A slower change then occurs, and the current may go through a minimum value i_{\min} before reaching the steady state i_{∞} .

From the moment electrolysis begins, an anode layer grows sideways, starting at many randomly spaced points. It is probably composed of CuCl, formed by the reaction $\text{Cu} + \text{Cl}^- \rightarrow \text{CuCl} + e^-$ and removed by the reaction $\text{CuCl} + \text{Cl}^- \rightarrow \text{CuCl}_2^-$. When the anode has become completely covered,

the layer is of the order of 10^{-4} cm in thickness. At this point an abrupt drop in i occurs (due to the sudden ϵ change). This is followed by a rise in resistance, which occurs when the pores are closed, and only slightly more CuCl is deposited than that necessary to cause the ϵ change. During the period when the high current was flowing a steep Cl⁻ gradient was established. The quick drop in i does not affect the over-all diffusion layer, and so the Cl⁻ continues to diffuse slowly toward the anode, building up the concentration. This will reduce the resistance of the layer, for it is more soluble in higher concentrations of Cl⁻. In the steady state the layer formation reaction proceeds at the same rate as the layer removal reaction, the net reaction being $\text{Cu} + 2\text{Cl}^- \rightarrow \text{CuCl}_2 + e^-$.

When the steady-state current is interrupted (V_∞ assumed to be greater than ϵ_{11}), V drops instantly from V_∞ to ϵ_{11} (an ir drop) then decays very rapidly to $\epsilon = -0.05$ v (an overvoltage decay) where it remains relatively constant. At the interruption r begins to decrease rapidly, presumably due to Cl⁻ attack on the outer part of the anode layer. When the decay of r is approximately 96% complete, the inner part of the layer apparently ruptures and ϵ drops abruptly from -0.05 v to -0.27 v (ϵ_1). After several seconds, depending on the value of V_∞ before interruption, the layer, whose thickness was of the order of 10^{-4} cm before interruption, is completely dissolved. As the concentration gradients in the anolyte gradually disappear, ϵ drops from ϵ_1 to ϵ_0 . Thereafter ϵ continues to drop slowly until it eventually reaches ϵ_0 .

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

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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, Theo-
retical Electrochemistry

Headquarters at the Sheraton-Gibson Hotel

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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 8, 29, 30, and 31, and November 1, 1956

Headquarters at the Statler Hotel

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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.



The Role of Science and Technology in Education¹

John T. Rettaliata²

Re-evaluation of Education

In a democracy, there can never be too much discussion and examination of the basic constituents of our way of life. We must continually evaluate and re-evaluate our institutions, honestly and with a critical eye, if they are to remain vigorous and meaningful.

Certainly, education is no exception. Indeed, education in many ways is the foundation of our democracy and its central pillar. Without it, the stirring words of Carlisle, Pitt, and Voltaire would not have spread across the seas to plant the hunger for liberty and equality in the souls of men and women in the American colonies and eventually in almost every other corner of the world.

Without education today, the flame these men and women so carefully fed and preserved for us would be lost to our children. Without education, our generation would not know the relative freedom from grinding physical toil that was the lot of most of our forebears. Without education, succeeding generations would be unable to profit from our failures and triumphs.

It is well, then, that we look critically at education and try to see in what ways it is or is not serving us and our democracy as it should.

Representing, as I do, an institution that is known primarily as a technological institution, I am going to discuss the place of science and technology in American education today.

Science and technology must be made an integral part of education in America, from grammar school up. We live in a world of technology, and we should be guilty of gross unrealism if we ignored that fact in any part of our educational programs.

Our entire lives are intricately involved in technology. Many of us find employment in industries and businesses that were unknown not too long ago. Where did they come from? You know the answer as well as I do—from our continually advancing technological skills.

Never before in all history has technology played so vital a part in the lives of men and women everywhere. Never before have so many persons, especially in this country, encountered in their everyday lives so many miracles of production and design—miracles that they have come to accept as a commonplace part of existence.

That is why I feel strongly that knowledge of science and technology and their places in our economy must be integrated into our educational programs. If we do not learn to understand our own developments, how can we learn to

manage them so that they will serve rather than destroy us? If we honestly hope to minimize poverty in our land and open up broad new avenues of opportunity and advancement for all people, how can we do anything else but continue a course that already has given us a standard of living unparalleled in the history of the world?

One fact is inescapable: technology is the keystone of our great economy. New products, new production processes are continually springing from our vast storehouse of technological know-how.

But this know-how does not perpetuate itself, any more than other worthwhile achievements do. It must be preserved in our educational institutions and there transmitted to the youth of our nation.

Functions of Education

These educational institutions, of course, serve other functions than merely passing on certain bodies of knowledge.

First, they continually increase mankind's store of knowledge. The backgrounds of most of the product and process inventions that underlie our modern world originated in the laboratories of universities around the world. At this very moment lights are burning late in laboratories, and new generations of men and women are grappling with problems the answers to which will constitute tomorrow's technology.

Second, it is the duty of our educational institutions to be concerned with the great responsibilities that go with great achievements. Technology has placed tremendous economic and military power in our hands. The extent to which we misuse that power represents, in large measure, the extent to which we are unprepared for it. If succeeding generations are to do better than we have done, it is our urgent business to educate them now for life in the kind of world where atomic energy and jet airplanes are commonplace.

I am sorry to say that, so far, we have made little progress in this direction. We are dealing with a relatively new concept when we speak of teaching responsibility for the consequences of our vast strides in material knowledge.

In the past, the university has generally provided a cloistered atmosphere. The ideal was for men to withdraw from active life so they could meditate and study. There was little opportunity for contact with the market place, and little opportunity for the market place to influence what was being taught within the ivory towers.

Even in American colleges this had usually been the common pattern for more than two hundred years. It still is a factor in American higher education.

But powerful forces have been at work, forces that have made inevitable a closer contact between the university, the

¹ This paper was prepared for delivery before the Electric Insulation Symposium at the Chicago Meeting, May 3, 1954.

² President, Illinois Institute of Technology, Chicago, Illinois.

market, the factory, and the farm. Perhaps the most important of these forces is the change in our way of living. It is largely as we have become a nation of cities that the necessity for partnership between education and industry has arisen.

We live in larger social units than our grandfathers did. Each segment of these large urban centers is dependent on other segments. What one part does or fails to do has a far-reaching effect on every other part.

It is the recognition of this interdependence by educators, industrialists, and businessmen that leads them to explore new and better ways of directing education and using the fruits of education for the greater good of all our people rather than the private gain of a few.

I consider it vitally important that they continue to do so, for lack of harmony and understanding between groups robs our material developments of much of their potential for good.

Need for Understanding

Lack of understanding is the basis of our present international tensions. It stands between us and the achievement of security, both economic and military.

It is at the root of our labor-management troubles; to some extent, it exists even on the university campus.

With America's entry into a technological era, both education and industry have undergone great change. Year after year, the demand has been for larger and larger facilities in science and engineering.

Universities have responded wholeheartedly to this demand, and in doing so they have to a large degree forsaken the cloistered way of life and come forth to meet the needs of industry in technological education and research.

And yet they have tended to become divided into two groups. On one side are those in the technological field, with their emphasis on measurable quantities. On the other side are those in the humanities and social sciences, whose interests are centered on ethical and cultural standards.

As each group became more firmly established, it came to have less and less contact with the other and consequently less understanding of the other.

I know that the technological institutions at one time tended to develop too narrow a view and to overlook social considerations. I am glad to say that this shortcoming has been largely corrected. Today there are definite programs for broadening the educational backgrounds of scientists and engineers. In line with that trend, Illinois Institute of Technology has modified its curriculum to give its students more economics, more history, more sociology, along with their technological studies.

Now let's look at the other side of the educational picture. How broad a view do students in the schools that emphasize the humanities and social sciences have of scientific and technological developments?

I am afraid that in many of their curricula the part technology plays in our lives is too often overlooked. I hope that those institutions will take steps to correct these shortcomings where they exist in their programs, even as we in the technological schools are striving to give our students a better balanced program.

I don't say that everyone should be an engineer or a scientist, even though it may sometimes seem to us that a thorough technical training is essential in a world of television sets, hydraulic brakes, and helicopters. Housewives, for example, with vacuum cleaners, dishwashers, washing machines, and other conveniences, probably operate more elec-

trical and mechanical equipment in the course of a day's work than a master mechanic did a generation ago. Be that as it may, I'm not going to recommend that a woman be required to present an engineering diploma when she applies for a marriage license.

Scientific and technological pursuits in themselves are still specializations, and no one can specialize in everything. Persons trained and experienced in other occupations will still be needed, as they always have been needed. But those who teach our children, manage our businesses, edit our newspapers, and run our factories should have some knowledge of the productive technology that makes our economy function.

Technology, applied to American industry, business, and agriculture, has created leisure time and material comforts that exceed the wildest dreams of anyone who lived a century ago.

The paradox of our time is that despite this progress we still find ourselves uneasy, dissatisfied, uncertain of the future. We face grave and trying problems at home and in many parts of the world.

Technology Develops Fears

Different persons blame this state of affairs on different causes. But underneath it all, it seems to me, is a misunderstanding of the role of technology in modern life.

Because of this misunderstanding we are surrounded by doubt and fear—fear of the machine, fear of change, fear of technological unemployment, fear of domination by large corporations.

These fears arise because technology is not well enough understood by the man and woman in the street. Particularly mysterious to them are the ways in which modern technical processes are brought into being and their products made available to the public. Let us examine this process briefly.

A technical development may have its beginning in a laboratory, but it benefits mankind only when it is taken out of the laboratory to serve some useful and constructive purpose.

This requires a financial risk, in many cases a very large financial risk. Thus, in our country, technological innovations reach the public through the medium of industry and business.

When we praise American technology for the wonders it has produced, we must also praise American business and industry. Neither could exist as we know it without the other. To praise technology and condemn industry is like praising milk but condemning cows. Yet there are those who manage to perform this trick of logic.

We must overcome our fear of technology. We can do so by the time-tried method of investigating it and its effects. Ignorance is the basis of most fears; it is the basis of this fear, too.

As important as facing up to the role of technology ourselves is our obligation to embrace it in our schools even as we teach history, philosophy, and the other cultural heritages that make our society what it is.

If we do this, we will not be a nation of people haunted by the fear that technology will cost us our jobs or bring about other unhappy consequences. We will see that even though the buggy-whip factory is extinct, we can get along without it in a society that employs 12,000,000 persons to make and service its automobiles.

Today our colleges and universities belong in the forefront

of a vigorous campaign to dispel the confusion that exists regarding technological development.

One effective way in which they could do this is by widening the base of both scientific and liberal arts curricula. Many are already doing so, but there is room for improvement.

In this technological age, of which every one of us is a part, it does not seem unreasonable to require each of our students in the arts and social sciences to have some background of technical study, at least enough so he can understand our dependence on technical advances.

When this is a part of his background and when, at the same time, the student of technology has a good grounding in the humanities and social sciences, I believe we shall produce generations of men and women far more capable of guiding their destinies than our generation has been. If it is true that we cannot ignore the past, it is just as true that misjudging technology amounts to turning our backs on the present and future.

The schools of technology must not overlook the lessons to be learned from evaluating the human and spiritual aspects of our civilization. Those in the fields of the humanities must have a basic understanding and appreciation of the part advancing technology is playing in the development of our nation if they are to contribute intelligently to the life of the nation.

Technology, fostered by our free institutions, has enabled us in America to build rapidly and well. Our maze of modern industry is only the superficial evidence of that building.

Increasing amounts of leisure time and increasingly higher standards of living have enabled our people to be schooled as no other people has ever been schooled, and knowledge begets the thirst for new knowledge.

We are a people who have been taught to aspire to better things that make life more exciting, more productive, more worth living, than it was in the past.

We have trained men and women alike to throw open closed doors, until it is a national doctrine that no threshold is uncrossable. We dare to believe that even the distant frontiers of other worlds will be crossed tomorrow.

We must not dwell too long on what has been done, impressive as that is. Our teachers and our students think more of what is waiting to be done.

We Americans number about 160 million persons today. Serving the 200 millions expected before the end of the century will demand the vast expansion of everything we have today in the United States.

From a technological point of view, such an expanded population will surely demand the opening up of untapped resources, the salvaging of natural treasures now buried deep in the oceans and seas. Such areas as Labrador and the polar regions must be made productive in some way.

Our children will search far and wide for substitute raw materials for industry, especially in our key resources—minerals and fuels.

They will develop marginal resources like the oil-shale seams of the Rocky Mountains. Atomic energy for peaceful purposes will follow. Perhaps energy can be taken directly from the sun to turn the wheels of industry and run the electric fan, the TV set, and the refrigerator in your home.

These things may sound fanciful today, but they will be absolute necessities tomorrow. Our production must keep pace with our expanding population lest our nation stagnate and die.

In our educational institutions, we have the means for transmitting and enlarging the body of knowledge needed to create and direct the technology of the future. Let us strengthen and preserve them.

Above all, let us not dispense education in packages, neatly wrapped to prevent contact with anything else. Let us strive to produce technologists with an awareness of the rich heritage of other fields of study, and arts students with an appreciation of the economic facts of life about this world in which we live.

By so doing, we will enrich our nation with capable people and with such resources we most assuredly will go on to attainment of ever great heights.

George W. Heise Receives Acheson Award

George W. Heise was awarded the Edward Goodrich Acheson Medal and Prize at a dinner held in his honor on Tuesday, October 5, 1954, during the 106th meeting of the Society at the Statler Hotel in Boston.

The Acheson Award is made for conspicuous "contribution to the advancement of any of the objects, purposes or activities" of the Society. Through the very breadth of the qualifications thus laid down by its founder, the senior medal of The Electrochemical Society has done high honor to any of its recipients.

George W. Heise was born on the shores of Lake Michigan in Milwaukee, Wisconsin, in 1888. There, he, a brother, and a sister grew up in a normal mid-western fashion, attending the public schools of Milwaukee. Exposing himself to the scientific training available there, he successfully completed his secondary schooling and entered a second—and very important, in view of later activities—phase of his career.

In the fall of 1905, Mr. Heise entered the University of Wisconsin and received the B.S. degree in 1909, the first year in which that degree was awarded for the four-year work in chemistry. It is easy to see how the seeds of enthusiasm for electrochemistry were planted during this period. Wisconsin in those days felt the influence of such forceful teachers as Louis Kahlenberg, known for his very positive, although perhaps not always successful, challenge of accepted theories of electrochemistry. There, too, was O. P. Watts, known for his contributions in corrosion and plating. It was at Wisconsin, also, that C. F. Burgess had organized a Department of Applied Electrochemistry and taught what was probably the first course in that subject in any American school. Of these associations Mr. Heise once said: "Fortunate indeed were those of us, not of the engineering school, who made the pilgrimage to the old Chemical Engineering Building to work in the applied electrochemistry laboratory



GEORGE W. HEISE

with Dr. O. P. Watts and to attend the lectures of Professor Burgess—where we discoursed learnedly on over-voltage, theories of corrosion, cathodic depolarization in primary batteries, and the fundamentals of organizing and financing an electrochemical enterprise."

Thus a broad interest in electrochemistry had been established when, in 1909, Mr. Heise left Wisconsin, apparently to continue an academic career, first going to Grinnell College for a year as instructor in chemistry, then to DePaul of Chicago for a second year during which he headed the newly organized Department of Physics, and was also responsible for the chemistry course for part of the time. While at DePaul he resumed graduate work in absentia in anticipation of his return

to Wisconsin the following year. It was during this period of temporary defection from Wisconsin that Mr. Heise spent a summer at the University of Chicago under R. A. Millikan. While there he translated into German for publication in *Physikalische Zeitschrift* Millikan's epic work on the charge of atmospheric ions, which later became the basis for the award of the Nobel Prize.

Returning to Wisconsin in 1911 for graduate study, Mr. Heise worked under Kahlenberg and served as assistant in the Department of Chemistry. He received the M.S. degree in 1912 and spent the next year as fellow in chemistry, continuing work in physical chemistry under J. Howard Mathews, with research with Watts in electro-deposition on the side.

Up to this point the Medalist's activities showed every sign of beginning a promising academic career. That it did not continue was a loss to the teaching profession, for in many respects he is a natural born teacher and his basic viewpoint and philosophy have always been those of a teacher. However, Mr. Heise left the academic world in 1913 on one of his several excursions into the field of public service.

He joined the Philippine Bureau of Science at Manila as physical chemist. In the course of four years he became Chief of the Section on Weights and Measures, Water Supply and Physical Chemistry, and part of the time served as Acting Chief of the Division of Inorganic Chemistry. Mr. Heise took over the chemical laboratory and field survey work on water supply as part of a general program which was carried out in cooperation with the Bureaus of Health and of Public Works and which had a profound effect on the life expectancy and public health of the Philippines. In addition, he worked on corrosion, photosynthesis, electroanalysis, and radioactivity of ground waters and sea water. Versatility of the work is evidenced by the appearance of a series of over 30 papers in the *Philippine Journal of Science* and in the *Journal of Physical Chemistry*.

Perhaps one of the very early urges to do something about the dry cell may have arisen at this time. The work on radioactivity of waters necessitated riding out on native ponies to reach remote locations, and all equipment had to be carried by porters, 40 lb to the man. Geiger counters hadn't been invented in Heise's day in the Philippines, and the method of measuring radioactivity was to observe the discharge of an electroscope. A large wet storage battery of several hundred cells, available in the laboratory for charging electroscopes, obviously could not be carried to location at 40 lb per man. The method of charging was, actually, to develop static by rubbing a piece of ebonite. Anyone, faced with the strenuous effort of rubbing a piece of ebonite with a mangy cat skin, perhaps in the midst of a tropical down-pour, would have both incentive and ample opportunity to dream up the very small, high voltage B batteries of today.

Serious influences of the Philippine phase were the associations with others in the Bureau at the time. Among these were R. R. Williams, of vitamin B

fame, Elmer D. Merrill, the botanist, and Marshall A. Barber, the biologist famed for his work on malaria. There also was W. E. Pratt, geologist who later became a vice-president of Standard of New Jersey, and in Heise's own group was A. S. Arguelles who ultimately served as Director of the Bureau of Science. Some of these professional ties formed in the Philippines have persisted up to the present.

Another permanent tie was formed by the Medalist during his service in the Philippines. In 1915 he married Margaret Armstrong, and their family was founded in the Islands. Their son, Dr. George A. Heise, is Assistant Professor of Psychology at Oberlin College. Their daughter, Dr. Margaret D., now Mrs. W. D. Stevens of New York, was Assistant Professor of Bacteriology at Ohio State.

While still in the Philippines, Mr. Heise became aware of the first rumblings of World War I, and offered his services in the Reserve Corps when this country threatened to become involved. Returning to the States soon after, he received his commission, then taught again for a few months at Wisconsin until called into active service. Thereafter, throughout this country's participation, he served in the Army; first as Captain in the Utilities Department of the Quartermaster's Corps, he was adjutant, later acting officer-in-charge, of utilities at Camp Grant, Illinois.

After about a year of service at Camp Grant, Mr. Heise was transferred, as Captain in the Chemical Warfare Service, to the chemical plant at Saltville, Virginia. There, at the time of his separation from the Army, he was in charge of research projects related to the fixation of nitrogen by the Bucher process.

Apart from the basic interest in electrochemistry, the deciding influence affecting his career after he came out of the Army may have been his acquaintance with the late Dr. R. C. Benner, well known as a member of this Society and as the Director of Research for the Carborundum Company. In earlier years Dr. Benner was associated with National Carbon Company, and it was he who gave Mr. Heise his first introduction to the industrial technology of the dry battery. This field has been the backbone, although far from the entire substance, of the Medalist's subsequent career.

During 34 years with National Carbon he served as department head for much of the research activity on the dry cell. He was largely responsible for the development and commercialization of air-depolarized cells, and made frequent and successful excursions into other battery fields, electrochemical synthesis, brine cell and porous carbon electrodes, special depolarizers, electrolytic condensers, as well as catalysts and sorbents.

Reviews of the early development of the dry cell have been covered, among other places, in Mr. Heise's address as President of the Society in 1948¹ and in review articles of 1952.² Suffice it to say that by the end of World War I a thriving industry had been established and radio was "just around the corner." Concepts of fineness, particularly as developed by Burgess, had opened up new vistas of service capacity for the miniature dry cell, without dependence on the expensive and erratic forms of artificial manganese dioxide then available, and important structural changes had been made, or were in the offing. Nevertheless, service was not generally considered a saleable feature; fundamental study had lagged, and only a small portion of the potential cell capacity was being realized.

The work of the Medalist should be viewed against this background. One of his early contributions was the development of a method of milling together the constituents of the dry cell bobbin, that is, depolarizer and carbon, which freed the dry cell for all time from the relatively expensive grades of graphite previously used, and also paved the way for what may have been the first commercial utilization of acetylene black in this country.

Much of his effort has also gone into fundamental investigation of the chemistry of the manganese system. This work by Heise and his colleagues, never completely interrupted at any time, has led, on the one hand, to more complete understanding of the reactions occurring in the dry cell, of their relation to depolarizing efficiency, of the distinct and characteristic functions of the electrolyte components such as zinc chloride and ammonium chloride, and of the crystallinity and other basic properties which are important in highly efficient manganese depolarizers. It also led, about 20 years ago, to an improved process for the electrolytic

¹ *Trans. Electrochem. Soc.*, **93**, 2P (1948).

² *This Journal*, **99**, 179C, 191C (1952).

production of manganese dioxide, which has had a major impact on the industry. This probably was the first such process successfully put into commercial production. Today, if any one factor can be considered pre-eminently responsible for the tiny and highly efficient dry cells in hearing aids, portable radios, and the like, it is probably the combination of electrolytically prepared manganese dioxide and acetylene black which made these possible.

Separators in the dry cell also received attention. Early work led to the introduction of kraft-type paper, now standard in some types of cells. More recently, with the advent of numerous resinous materials, Heise and his co-workers have developed thin resinous films which, unlike the older cereal paste and paper separators, combine extreme stability toward the chemical attack of manganese dioxide with almost ideal diffusion characteristics and high mechanical strength. These also are becoming standard in some types of cells. All in all, dry cell efficiency has increased more than threefold during the Medalist's career, much of it due to the work of his group.

Mr. Heise's activities covered battery systems other than those using manganese, foremost among these the Lalande and the alkaline air-depolarized cells. The fourfold increase in capacity of these alkaline batteries since 1920 is almost entirely due to this same group of workers. In the air-depolarized cell, zinc is oxidized by atmospheric oxygen at a carbon electrode. Long desired as a substitute for cells containing solid depolarizer, such as the copper oxide of the Lalande cell, several forms had appeared from about 1890 on. However, Mr. Heise was largely responsible for much of the research that transformed these earlier versions into the present commercial cell, outstanding for its constant voltage, and perhaps representing the most efficient of the commonly used galvanic systems. More recently the air-depolarized cell has been dried up, like the manganese cell, and reduced in size for use in hearing aids and the like.

Other gaseous depolarizers were not overlooked. The substitution of pure oxygen for air as depolarizer has permitted the development of an electrode capable of operation at more than 300 amp/ft². Similarly, hydrogen, chlorine, sulfur dioxide, carbon monoxide, hydrazine, and other gases were considered as depolarizers, both for use in

batteries and for electrosynthesis. The work permitted construction of cells which were unique in that gases constituted the active elements at both electrodes, for example, hydrogen-oxygen, hydrogen-chlorine, sulfur dioxide-chlorine, carbon monoxide-oxygen. One important outgrowth of these studies was a chlorine depolarized battery which attracted considerable attention during World War II for heavy duty service, and which today remains among the most attractive of electrochemical systems when a high yield of energy from a minimum weight and volume is required.

The Medalist has been active in other electrochemical fields also. The development of a process for making electrolytic manganese dioxide, now recognized over other synthetic forms as the most desirable battery depolarizer has already been noted. The success of this program depended in large part on obtaining an improved graphite anode sufficiently resistant to anodic attack in acid manganese sulfate electrolyte. A suitable anode came from researches under Mr. Heise's supervision in the field of brine electrolysis and is now available to all makers of electrolytic oxide.

The work on brine electrolysis covered not only the graphite anode, but also process factors. Mr. Heise's group made substantial contributions to the better understanding of such factors as solution composition, current density, temperature, etc. Their results have led to improved anode performance.

Mr. Heise has always demonstrated outstanding talent, not only in achieving practical objectives, but also in recognizing the basic advantages and theoretical possibilities of new technical tools. An example of this talent was his ability to foresee that carbon of controlled porosity, manufactured primarily for gas diffusion and filter applications, had attractive possibilities as electrode material. On the practical side, it permitted continuous operation; on the theoretical side, it offered, in a sense, a stationary substitute for rapidly rotating electrodes or other mechanical devices, thereby partially removing limitations imposed by diffusion on all electrochemical processes. Based on these considerations, a number of potentially useful applications of porous electrodes were carried out, several of which have been described in the literature of this Society. Among these should be mentioned the electrowinning of

copper, in which the use of the porous electrode can, under some conditions, reduce power requirements by more than half. Similarly, iron can be recovered from its ores or from waste pickle liquor. In the electro-organic field, the work of Heise's group showed porous electrodes could in large measure overcome the difficulties inherent in handling insoluble depolarizers or in recovering unstable products. Oxidation and reduction of inorganic chemicals, production of hydrogen peroxide from the oxygen of air, and conversion of sulfur dioxide to sulfuric acid were also among the researches on the porous electrode.

A measure of the Medalist's career can, perhaps, be obtained from a count of 45-50 publications, many of the papers having appeared in the *TRANSACTIONS* and *JOURNAL* of this Society, in addition to about 85 patents.

In describing these technical contributions, chronology has been of minor importance. To pick up the chronological thread, return to the years of World War II when Mr. Heise again rendered public service. He served as head of a group on a contract project with the National Defense Research Council and Chemical Warfare Service. The group was charged with the responsibility of producing from a domestic source a sorbent carbon suitable for the small, light-weight canisters then in use. This group made substantial contributions to the understanding of the relation between the structure of sorbent, or "activated," carbon and the high rates of sorption required for the thin layers of the modern canisters used by the military. The project was successfully brought to the level of a plant process for production of a good carbon without dependence on imported raw materials.

Closely related to this work on gas mask carbon was the development of so-called "catalytic" carbon, which has been described in part in the *JOURNAL*. In this project, Mr. Heise and his colleagues defined the acid counterpart of the alkaline system on which the air-depolarized cell is based, and showed that sorbent-type carbons can be modified so that they will sorb oxygen from the air in the form of an active carbon complex which can be used for chemical oxidations. In contact with such "catalytic" carbons, substances otherwise unaffected, such as sulfur dioxide, can be oxidized by atmospheric oxygen.

A year ago last July Mr. Heise reached the age conventionally referred to as "retirement" age. In this particular case, it was more a matter of "time for a change." He has continued his activities in batteries and allied fields. In addition to private consulting, which keeps him on the go, he serves the Committee on Undersea Warfare of the National Research Council as Chairman of the Panel on Primary Batteries.

No tribute to the Medalist would be complete without mention of his activities in professional societies. Long a member of The Electrochemical Society and active on many of its committees, he served as Vice-President in 1935-1936 and again in 1946. As President in 1947-1948 he carried the Society through a difficult transition period. At the section level, he was one of the founders and later Chairman of the Cleveland Section and has been a frequent speaker on electrochemical subjects before various Local Sections. He is a Fellow of the American Association for the Advancement of Science, and a member of the Faraday Society, the Society of Chemical Industry, the American Chemical Society, and Alpha Chi Sigma. He is a Registered Engineer in the State of Ohio, and his professional status is further attested to by authorship, now continued through several editions, of the primary battery section of the Encyclopedia Britannica. Among honorary scientific societies, he belongs to Sigma Xi and Phi Lambda Upsilon.

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1955 BOUND VOLUMES.

Members and subscribers who wish to receive bound copies of Vol. 102 (for 1955) can receive the volume for the low, prepublication price of \$6.00 if their orders are received at Society Headquarters, 216 West 102 Street, New York 25, N. Y., by December 1. After that date members will be charged \$12.00 and nonmembers, including subscribers, \$18.00.

NEWS ITEMS

Graduate Science Fellowships Offered by National Science Foundation

About 800 students with special abilities in science will be selected for a year of graduate scientific study during the academic year 1955-1956 in the National Science Foundation's Fourth Annual Graduate Fellowship Program. The closing dates for receipt of applications are December 20, 1954, for postdoctoral applicants, and January 3, 1955, for graduate students working toward advanced degrees in science. The selections will be announced on March 15, 1955.

National Science Foundation fellowships are awarded to United States citizens who will begin or continue their studies at the graduate level in the life and physical sciences (including interdisciplinary fields) during the 1955-1956 academic year.

Selections will be made solely on the basis of ability. The majority of the fellowships will go to graduate students seeking master's or doctor's degrees in science, although about 100 awards will be made to postdoctoral applicants. Science students who are now college seniors are encouraged to apply for the awards.

The rating system for selection of predoctoral Fellows will be based on: (a) scores on tests of scientific aptitude and achievement, (b) academic records, (c) written evaluations of each individual from his faculty advisors and other qualified observers. Postdoctoral applicants will not be required to take the examinations. Applicants will be rated by special Fellowship Panels, established by the National Academy of Sciences. Final selection will be made by the National Science Foundation.

Stipends for National Science Foundation graduate fellowships will vary with the academic status of the Fellows, from \$1400 to \$3400 per year. Dependency allowances will be made to all married Fellows. Tuition and laboratory fees and limited travel allowances will also be provided.

National Science Foundation Fellows may attend any accredited nonprofit institution of higher education in the United States or similar institutions abroad.

Applications for the 1955-1956 National Science Foundation Fellowship Program may be obtained from the

Fellowship Office, National Research Council, Washington 25, D. C.

Mercast Forms New British Firm

Admiral Alan G. Kirk, Chairman of the Board of the Mercast Corporation, New York City, has announced that this company and Guest, Keen and Nettlefolds Limited, London, have jointly formed a British company, Mercast (Great Britain) Limited, to license the use of the Mercast process to firms in the United Kingdom and the British Commonwealth (excluding Canada).

The process, already gaining wide application in the United States, utilizes frozen mercury to form the expendable patterns for producing parts by the investment casting process. Since its development several years ago, it has enabled the precision casting of larger and more complex parts than were theretofore possible. Important uses for the process include components for the aviation industry and for atomic energy work. In addition, such parts as turbine blades, wave guides, pneumatic piston components, locking and hatch devices, generator and motor brackets, impellers, glass mold dies, and many other products have been successfully produced by the process.

American Mercast licensees include Alloy Precision Castings Company, Kolcast Industries, Inc., and Thompson Products, Inc., all of Cleveland.

American Directors of the new British firm include, in addition to Admiral Kirk, S. J. Sindeband, President of Mercast. The Chairman of the new company and other Directors represent British interests.

Bell Labs. Develops New Transistor

The time when home television sets will use tiny transistors about the size of pencil erasers instead of a large array of vacuum tubes came closer to realization with the recent announcement by Bell Telephone Laboratories of a transistor which will operate at 440 million cycles, higher in frequency than any transistor yet known.

Bell Laboratories, where the original transistor was invented, unveiled its latest member of the family of the "mighty mites" with a talk by Dr. J. M. Early before the Western Electronics Show and Convention at Los Angeles, Calif. Dr. Early invented the new transistor and was assisted in its development by W. C. Hittinger and Dr. J. W. Peterson.

Bell scientists foresee its use in portable radio sets, the transcontinental radio relay system, and submarine telephone and television cable repeaters. Used in military equipment, the device could be of tremendous importance to national defense.

The ultra-high-frequency device, called an "intrinsic Barrier" transistor, can increase an electrical signal a thousandfold. In addition to its ability to amplify signals, it may be used as a generator of electrical oscillations. The new device, like other junction transistors, can operate at extremely low power. But, unlike earlier transistors, it can also operate at relatively high power. Although the new transistor is still in the experimental stage, frequencies as high as 440 million cycles per second have been generated to date.

New Fluorine Cell to Aid Uranium Program

A boost for fluorine output, available in connection with the uranium 235 separation program, has been made possible through the development of a fluorine cell of advanced design by engineers of Union Carbide, operator of the uranium separation plants at Oak Ridge, Tenn., and Paducah, Ky., for the Atomic Energy Commission. This development was described recently at the Symposium on Fluorine conducted as a part of the American Chemical Society's national meeting at the Hotel Statler in New York. The description of the new fluorine cell was given by G. H. Montillon, a Carbide engineer. Co-authors of the paper were J. Dykstra, S. Katz, C. B. Clifford, and E. W. Lowell.

Known as a "medium-temperature electrolytic fluorine cell," it has considerably advanced in detailed design and maintenance techniques the method of obtaining fluorine, essential in producing the atomic fuel, uranium 235. It produces fluorine at lower cost, in less operating time, and at a much higher rate. It has doubled the life of previously available cells.

Since the new cell holds the promise of being adaptable for use in industrial processes generally, Carbide engineers have projected the idea into a typical plant to produce two tons of fluorine daily. Their description is based on the operation of a 36-cell unit. Description in full detail of the new cell design and of the operation of the unit is in line with the Nation's program of bringing developments in the atomic energy field to the attention of industry.

17-Year Oxide Batteries

Storage battery users recently caught a fleeting glimpse of the industry's massive research effort when The Electric Storage Battery Company briefly lifted a veil of secrecy and revealed the existence of batteries lasting more than seventeen years. Previously seven years had been the best life normally attainable in the same service.

The company presented these battery performance records to the U. S. Patent Office several months ago in support of its sweeping claims for patent protection on new and improved battery grid alloys. Neither the firm nor the patent office made any announcement of the seventeen-year batteries. Only when the patents were awarded and published recently did the actual case histories become available to the industry for study.

The recently granted patents describe the alloying of lead with varying and precisely controlled quantities of antimony, arsenic, and silver, and use of these alloys in the grid structure of battery plates.

According to the patent, the seventeen-year case histories describe batteries maintained on "float," as in hundreds of industrial applications, including emergency lighting, switchgear control, fire alarm systems, telephone stand-by, railway signal control, and other stationary power applications requiring stand-by current. The company feels the new developments will have a significant effect on the service life of Oxide storage batteries in all other industrial applications.

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

Notice to Members

By now you have received your official voting ballot from Society Headquarters. If you have not already done so, please return the ballot by *December 15* so that your vote may be included in the final election count.

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 (preferably by November 15) 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.

In order to have a balanced agenda, it will be desirable to have a review paper of the status of each field, half-hour presentations of new information which can be scheduled by midwinter 1954, and a number of ten-minute presentations of the "late news" type.

Anyone wishing to present a paper at this symposium should contact F. J. Biondi, Bell Telephone Laboratories, Murray Hill, N. J., preferably by November 15, but not later than December 1, signifying interest in participating and title of proposed papers. This information is needed to plan the symposium.

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 contribu-

tions 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.

NEW MEMBERS

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

Active Members

MANUEL BEN, General Motors Corp., mail add: 13430 Rosemary Blvd., Oak Park 37, Mich. (Corrosion, Electrodeposition)

FRANK J. BIONDI, Bell Telephone Labs., Murray Hill, N. J. (Electronics)

EMANUEL L. BRANCATO, Naval Research Lab., mail add: 5707 47th Ave., Riverdale, Md. (Electric Insulation, Electrodeposition, Electronics, Theoretical Electrochemistry)

PHILIP CRISPINO, Foster D. Snell Inc., mail add: 1341-43rd St., Brooklyn 19, N. Y. (Battery, Theoretical Electrochemistry)

JAMES LESLIE CURTIS, Marathon Paper Mills of Canada Ltd., mail add: 9 Drake St., Marathon, Ontario, Canada (Industrial Electrolytic)

JOSEPH DE MILIA, U. S. Naval Gun Factory, mail add: 4812 41st St. N. W., Washington 16, D. C. (Electronics)

JULIAN J. DRAVIS, Canadian Westinghouse Co. Ltd., Sanford Ave. N., Hamilton, Ontario, Canada (Industrial Electrolytic)

LINDSAY DUNHAM, Ets. Daniel Doyen S. A., 31-32 Blvd. du Midi, Brussels, Belgium (Battery)

OTTO H. FENNER, Monsanto Chemical Co., 1800 South Second St., St. Louis 4, Mo. (Corrosion)

PHYLLIS E. FOWLE, Aluminum Co. of America, mail add: 304½ Charles Ave., New Kensington, Pa. (Theoretical Electrochemistry)

GUNNAR L. GABRIELSON, AB Tudor, Nöl, mail add: Friggagatan 25 A, Göteborg C, Sweden (Battery, Electrodeposition, Theoretical Electrochemistry)

WILLIAM C. HANNAH, Ball Bros. Co., mail add: 2 Elizabeth Ave., Muncie, Ind. (Battery)

NAAMAN H. KEYSER, Battelle Memorial Institute, 505 King Ave., Columbus 1, Ohio (Electrothermics and Metallurgy)

ERICH LAUE, MacDermid Inc., mail add: Plungis Rd., Watertown, Conn. (Corrosion, Electrodeposition, Theoretical Electrochemistry)

NATHANIEL H. LIEB, Star Dental Mfg. Co., Inc., mail add: 5216 Lebanon Ave., Philadelphia 31, Pa.

FRIDERICK R. MEYER, Southern New England Telephone Co., Administration Bldg., 227 Church St., New Haven, Conn. (Corrosion)

ARTHUR R. NASRALLAH, Goodyear Aircraft Corp., mail add: 2233-25th St. S. W., Akron 14, Ohio (Corrosion)

BIAGLIO PESCE, University of Rome, mail add: Laboratorio di Chimica Fisica del l'Università, Rome, Italy (Theoretical Electrochemistry)

ARTHUR G. PIERDON, Art Metal Finishing Co., mail add: 5331 42nd St. N. W., Washington 15, D. C. (Electrodeposition)

EUGENE C. RAGATZ, Allen-Bradley Co., 136 W. Greenfield Ave., Milwaukee 4, Wis. (Electronics)

ÅKE HENRY L. ROSENDAHL, AB Tudor, Nöl, Sweden (Battery)

ALAN B. ROTHMAN, Westinghouse Electric Corp., mail add: 5624 5th Ave., Apt. C-8, Pittsburgh 32, Pa. (Theoretical Electrochemistry)

PAUL RUETSCHI, Louisiana State University, College of Chemistry, Baton Rouge, La. (Battery, Theoretical Electrochemistry)

SIDNEY M. SELIS, Diamond Ordnance Fuze Labs., mail add: 12408 Dalewood Dr., Silver Spring, Md. (Theoretical Electrochemistry)

THOMAS J. VINCENT, General Electric Co., mail add: 1099 Ivanhoe Rd., Cleveland 10, Ohio (Electronics)

OTTO J. VONDRAK, Kaiser Aluminum & Chemical Corp., mail add: 4618 Gaines St., New Orleans, 22, La. (Industrial Electrolytic)

WILLIAM G. WALLACE, Aluminum Co. of Canada, mail add: 196 Radin Rd., Arvida, Quebec, Canada (Industrial Electrolytic)

RAYMOND WARD, General Electric Co., Industrial Heating Dept., Rm. 105, Bldg. 96, Schenectady, N. Y. (Electrothermics and Metallurgy)

Associate Members

GEORGE B. COBEL, Dow Chemical Co., Bldg. 228, Midland, Mich. (Electro-

thermics and Metallurgy, Industrial Electrolytic)

HERBERT B. FISHMAN, General Dynamics Corp., mail add: 258 Lower Blvd., New London, Conn. (Corrosion, Electrodeposition)

PHILIP T. GREEN, Panama Canal Co., mail add: Box 213, Balboa, C. Z. (Electric Insulation)

RANKO SAMANTO ROY, Khallikote College, Berhamper, Ganjam District, Orissa, India (Theoretical Electrochemistry)

Student Associate Member

JOHN D. HORA, Inland Steel Co., mail add: 7034 Colorado Ave., Hammond, Ind. (Electrodeposition)

Reinstatements—Active

ANTONIO SCORTECCI, Istituto Siderurgico Finsider, Corso F. M. Perrone 24, Genova, Cornigliano, Italy (Electrothermics and Metallurgy)

ROBERT D. WILLIAMS, Fulbright Labs., Inc., mail add: P. O. Box 1284, Charlotte, N. C. (Corrosion, Theoretical Electrochemistry)

Reinstatement—Associate

R. R. WITHERSPOON, Army Chemical Center, mail add: Pvt.—U. S. 55435664, 9710TSO, ACml C Det. 2, Army Chemical Center, Md. (Battery)

Transfers to Active

THEODORE A. HIRT, Pittsburgh Steel Co., mail add: 654 Elm Rd. N. E., Warren, Ohio (Electrodeposition)

WILLIAM W. GULLETT, Chicago-Delaware Co., mail add: 6903 Baltimore Ave., College Park, Md. (Battery)

GEORGE L. SCHNABLE, Philco Corp., mail add: 36 S. Wyomissing Ave., Shillington, Pa. (Electronics, Theoretical Electrochemistry)

Transfers to Associate

ATTILIO L. BISIO, American Smelting & Refining Co., mail add: 25-20 21st St., Astoria 2, N. Y. (Corrosion, Electrodeposition)

JAMES CHRISTIAN LAMB, III, Mass. Institute of Technology, mail add: 15 Appletree Lane, Lexington, Mass. (Corrosion)

YEN-NGEN WANG, Crane Co., mail add: 3724 Washtenan Ave., Chicago 32, Ill. (Corrosion, Electrodeposition)

Resignations

J. E. HAWKINS, Dept. of Chemistry, University of Florida, Gainesville, Fla.

ECS Membership Statistics

The following two tables give breakdown of membership as of Oct. 1, 1954. The Secretary's Office feels that a regular accounting of membership will be very stimulating to membership committee activities. In Table I it should be noted that the totals appearing in the right-hand column are *not* the

sums of the figures in that line since members belong to more than one Division. But the totals listed are the total membership in each Section, with the exception that Sustaining Memberships are not broken down by Sections or Divisions. Since Sustaining Members are not broken down by Sections or Divisions, the total listed in Table I will be less than the total in Table II, the difference being the total number of Sustaining Memberships.

TABLE I. ECS Membership by Sections and Divisions

Section	Division											Total As of 10/1/54	Total As of 7/1/54	Net Change
	Battery	Corrosion	Electric Insulation	Electrodeposition	Electronics	Electro-Organic	Electrothermics & Met.	Industrial Electrolytics	Theoretical	No Division				
Chicago	12	32	3	48	11	8	8	8	17	10	100	104	-4	
Cleveland	37	34	5	48	29	7	19	25	39	11	152	153	-1	
Detroit	6	18	6	33	5	7	4	3	19	11	67	65	+2	
India	6	5	3	13	3	4	6	17	6	4	34	33	+1	
Midland	6	13	0	6	1	2	5	13	6	3	36	35	+1	
New York	59	102	18	129	70	30	46	55	79	57	403	404	-1	
Niagara Falls	4	15	0	14	3	7	41	41	12	14	109	109	0	
Pacific Northwest	5	10	0	7	3	2	5	12	9	4	31	31	0	
Philadelphia	23	26	6	33	41	17	16	14	37	23	154	153	+1	
Pittsburgh	3	25	4	17	7	5	19	13	21	10	69	69	0	
San Francisco	7	10	1	15	7	3	6	14	10	4	42	39	+3	
Washington-Baltimore	33	34	11	27	14	3	14	14	27	9	99	99	0	
Ontario - Quebec	7	11	0	13	0	3	16	19	7	13	45	40	+5	
U. S. Nonsection	66	159	27	170	93	56	95	104	149	80	632	622	+10	
Canada Nonsection	0	2	0	0	0	3	1	0	0	0	5	52	-47	
England	6	8	2	10	4	3	6	8	8	17	38	37	+1	
Foreign Nonsection	19	29	4	40	14	17	21	39	42	47	145	143	+2	
Total as of 10/1/54	299	533	90	623	305	177	328	399	487	317	2161			
Total as of 7/1/54	299	533	88	621	299	178	326	397	478	318		2148		
Net Change	0	0	+2	+2	+6	-1	+2	+2	+9	-1				

HAROLD LUNDIN, 6515 Blvd. East, Apt. 7D, West New York, N. Y.

LYNNE G. WIENENMANN, 503 17th Ave., East Moline, Ill.

JOHN K. WERNER, Bldg. 5, Apt. B5, 100 Franklin St., Morristown, N. J.

RALPH L. HORST, JR., 4842 Ellsworth Ave., Pittsburgh, Pa.

TABLE II. ECS Membership by Grade

	Total As of 7/1/54	Total As of 10/1/54	Net Change
Active	1895	1911	+16
Delinquent	90	83	-7
Life	14	14	0
Emeritus	34	35	+1
Associate	73	74	+1
Student	37	39	+2
Honorary	5	5	0
Sustaining	103	103	0
Total	2251	2264	+13

PERSONALS

WILLIAM J. KROLL of Corvallis, Oreg., has been awarded a Francis J. Clamer Medal by The Franklin Institute of the State of Pennsylvania. Dr. Kroll was out of the country at the time and the award was made in absentia, to be formally presented to him at a later date. The Institute honored Dr. Kroll "In consideration of his invention of a method adaptable to the large scale production of cold malleable

commercially pure titanium and zirconium," as reads the citation to the award.

WILLIAM E. TRAGERT, formerly a student at Yale University, has joined the staff of the General Electric Research Laboratory, Schenectady, N. Y., as Research Associate.

CHARLES G. HARFORD has recently been transferred from the Cambridge laboratories of Arthur D. Little, Inc., to



CHARLES G. HARFORD

San Francisco, where he is Technical Director of the ADL Western Laboratory Division which was opened in June of this year. This division will provide research facilities for ADL's western clients. While with the company in Cambridge, he worked on many varied projects, including coating compositions for coal, uses for gold and platinum, causes for staining in Vermont marble, corrosion problems, and research on the manufacture of fluorine. His work has resulted in more than 20 patents.



CLARENCE G. OZAR

CLARENCE G. OZAR has accepted an appointment with the Detrex Corp., Detroit, Mich., as Liaison Chemist in Metal Cleaning and Finishing. His responsibilities are to provide technical information and assistance between research laboratories and sales and service technicians throughout the country. Formerly, Mr. Ozar was Service, Development, and Research Chemist in Metal Cleaning with the Cowles Chemical Co., Cleveland, Ohio.

PAUL H. CARDWELL, previously Laboratory Director at Dowell, Inc., a sub-

siary of the Dow Chemical Co., Tulsa, Okla., is now engaged in basic and nuclear research with the Dow Chemical Co., Midland, Mich.

ERWIN F. LOWRY, Manager of the Lighting Engineering Laboratories of the Lighting Division of Sylvania Electric Products Inc., Salem, Mass., recently received the 1954 Illuminating Engineering Society Gold Medal, highest honor in the lighting field. The medal has been awarded annually since 1944, except in 1951 and 1953, for meritorious achievement conspicuously furthering the profession, art, or knowledge of illuminating engineering. Dr. Lowry is the first physicist engaged in light source research chosen to receive the society's medal. Nearly 30 patents have resulted from Dr. Lowry's research, almost all of which are related to gaseous discharge devices, especially cathodes. Most of his contributions to the art and science of lighting are found in the development of the fluorescent lamp.

WILLIAM N. DUNLAP was recently appointed Chief Chemist and Laboratory Director of the Reynolds-Robson Supply Co., Philadelphia, Pa. He was

previously employed as Project Engineer with the Friez Instrument Division of the Bendix Aviation Corp. in Baltimore, Md.



W. W. SELLERS

W. W. SELLERS has been appointed head of the Electrochemical Section of the Bayonne, N. J., Research Laboratory of The International Nickel Co., Inc. Mr. Sellers joined the staff at the Bayonne Laboratory in 1944 as Research Chemist. His work has been chiefly in the electrodeposition of nickel and nickel alloys, in which field he has published several technical papers.

BOOK REVIEWS

PROCEDURES IN EXPERIMENTAL METALLURGY by A. U. Seybolt and J. E. Burke. Published by John Wiley & Sons, Inc., New York, 1953. xii plus 340 pages, \$7.00.

A perennial problem to the book reviewer is the avoidance of clichés. This is one of those volumes which leaves little alternative. In brief, this book will find a ready audience, will meet with an enthusiastic reception, fulfill a long-felt need, is authoritatively written, will be a constant reference, should be in everyone's library, will serve the needs of student and research worker alike.

Most of these statements are, moreover, really applicable, however useless to the prospective purchaser. For the latter's sake, we should be more specific. "Procedures in Experimental Metallurgy" is just that, a reference-text-handbook on the experimental art, doing for the metallurgist what the classical Strong volume has done for the physicist. It covers the practical requisites that the student or laboratory apprentice is more often expected to

absorb by telepathy, osmosis, or simple exposure.

The content of the book is best described by its authors: "The preparation of metal samples up to the point of making observations on the metal." Accordingly, it begins with furnaces of all types and temperature measurement and control, and includes refractories; atmospheres; melting, casting, and heat treatment; fabrication; and powder metallurgy. It concludes with chapters on the preparation of pure metals and of single crystals. The authors have wisely elected to omit any consideration whatsoever of optical and diffraction metallography as being a separate field, so that even metallographic preparation is not included.

The authors' own experimental work attests to their competence to write the book, and the writing itself attests intimate acquaintance with the laboratory bench. Throughout, a given procedure is described in successive terms of principle and purpose, reduction to practice, and the more prominent pit-

falls. The information they impart is of eminently practical nature. The section on leak hunting in vacuum systems, for example, will strike many sympathetic chords.

A reviewer's criticism often resolves into what he would have done differently had he been the author. This one, out of painful experience, would have given more than negligible attention to parasitic emf's in potentiometer circuits, and would want more detailed description of the principle and operation of commercial recorders and controllers—a section on "what to do until the service man arrives." This is how encyclopedias get compiled. He also, with a genuflection toward the organization which pays his salary, might wish the book had been delayed long enough to permit more than casual description of zone-melting and zone-levelling procedures.

A closing note of wistful regret: Our current texts are being competently illustrated, but with a slick, conventionalized technique suggesting a publisher's anonymous assembly line. The information is conveyed, perhaps more clearly than ever before, but that is all. One can suppose it should be enough. But nothing else of the kind carries either the conviction or the charm which Roger Hayward's drawings have granted the Strong "Procedures." Such are what Seybolt and Burke deserve.

R. G. TREUTING

RARE METALS HANDBOOK. Edited by Clifford A. Hampel. Published by Reinhold Publishing Corp., New York, 1954. 657 pages, \$12.00.

This book, written by thirty-four specialists, is one that metallurgists, chemists, and engineers will find useful. It contains a wealth of up-to-date information, well systematized and readily located, about more than thirty-five metallic elements. Some of these—titanium, uranium, hafnium, and germanium—are but now acquiring prominence on the industrial stage. Others, such as manganese, tungsten, and vanadium, are old in use but have recently attained new stature. A book dealing with the "rare metals" has been badly needed for years; and now within twelve months two books, this and "Modern Uses of Nonferrous Metals," have appeared. The books, while covering some of the same elements, are more complementary than competitive.

The term "rare" in the title is not a happy choice, as the editor appreciates,

1955 BOUND VOLUMES

Members and subscribers who wish to receive bound copies of Vol. 102 (for 1955) can receive the volume for the low, prepublication price of \$6.00 if their orders are received at Society Headquarters, 216 West 102 Street, New York 25, N. Y., by December 1. After that date members will be charged \$12.00 and nonmembers, including subscribers, \$18.00.

and was used for want of a better adjective. It is intended to carry the metallurgist's connotation, "relatively scarce," i.e., excluding the thirteen "common" metals.

For the most part, each chapter discusses one element and the information about the various elements is arranged similarly in each, thus making it easy to use the book as a reference work. In the typical chapter a paragraph is devoted to each of the following: occurrence, production statistics, economics, derivation, physical and chemical properties, fabrication techniques, alloys, and present and potential uses. Variations in the care of preparing each chapter are to be expected and have been found. For example, in the chapter on beryllium a paragraph is repeated substantially verbatim, and "high electrical-high conductivity" is ascribed to beryllium copper alloys.

The bibliographical references at the end of each chapter are much more extensive than are usually found in such a work and add greatly to the value of the book. There are, for example, 389 references on uranium alone. The last chapter, giving tables of comparative data, is not only useful, but most interesting to peruse and constitutes a valuable feature.

The typography is good and the book seems sturdily bound in keeping with the usage that it might be expected to receive.

This reviewer likes the book and believes that it will be well received by those for whom it is intended.

E. E. SCHUMACHER

ELECTRICAL BREAKDOWN OF GASES by J. M. Meek and J. D. Craggs. Published by the Oxford University Press, Amen House, London E.C. 4, 1953. 507 pages, \$10.50.

The study of electrical discharges is one of the oldest in science. It has attracted many able researchers and one

statesman-scientist who took considerable personal risk in determining the extent of the electrification of rain clouds with such simple apparatus as a key and a kite. "Electrical Breakdown in Gases" has been written by two of these able researchers. The preface states that the writers hope that the book will serve as a research tool for those "engaged in fundamental studies of the growth of electrical discharges in gases, but . . . (to) be of use to those concerned with the development and application of gas-filled electronic tubes, with gaseous dielectrics, etc."

The work begins with a chapter on the fundamental processes in discharges, the emphasis being on the mechanisms most often encountered in the various classes of electrical breakdown. This chapter includes discussions concerning the collision cross sections of simple atoms and molecules for elastic and inelastic collisions, as well as subjects such as electronic and ionic mobilities. Experiments dealing with photo ionization, electron attachment, and detachment are also covered. The remaining eleven chapters proceed quite logically to cover the phenomena which one would be likely to observe in time sequence as the current across a gap filled with a gas slowly increases.

The predominant interest of the book is in the transient processes of the discharge. These transient processes are the Townsend discharge or spark and the transition region between the spark and glow, and between the glow and the arc. A detailed estimate of the theories of the sparking mechanism is set forth in Chapter VI. The streamer mechanism of the spark which has produced some quite considerable discussion is delved into, as well as its criticism. Although the discussion will undoubtedly continue, it is desirable that the arguments both pro and con be collected and expounded in one place.

The subjects of lightning and corona, time lags, and the growing technical importance of heavy molecules as insulating gases are brought together for the first time. As a work which is a compilation of present knowledge of a complicated subject, "Electrical Discharge in Gases" suffers from a need, difficult to fulfill, to tie together its diffuse elements. A chemist or physicist will perhaps desire more elucidation from the standpoint of the atomic and electronic structures involved in the discharge, as well as a more generally critical approach to the many papers mentioned.

The book will probably be of greater use to those interested in the applied aspects of the discharge than to those delving into the fundamental problem.

KENNETH B. McAFEE, JR.

RECENT PATENTS

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

August 3, 1954

Cusano, D. A., and Studer, F. J., 2,685,530, Method of Preparing Transparent Luminescent Screens

Rodda, S., 2,685,531, Light-Sensitive Electron-Emissive Electrode

Gauthier, G. G., 2,685,563, Anodic Oxidation of Aluminum

Emmett, R. A., Jr., and Petering, W. H., 2,685,564, Electrolytic Cleaning Process

Jones, L. V., Willis, S. J., and Perry, M. M., 2,685,565, Filtering and Cleaning Means

Schmitt, H., 2,685,566, Molten Metal Electrolysis Cells

Support Our Advertisers

Since advertisers in the JOURNAL are investing money in our publication, members of the Society have a great opportunity to cooperate in the mutual success of the project. For instance, Society members buy large quantities of products, instruments, and equipment. Whenever an advertiser's products meet company specifications, readers are urged to give preference in their purchases to JOURNAL advertisers.

Justi, E., 2,685,608, Thermoement,

Particularly for the Electrothermic Production of Cold

Vuignier, M. A., 2,685,678, Quick Release Battery Terminal Clamp

August 10, 1954

Cory, G. L., 2,686,142, Method of Manufacturing Corrugated Microporous Separators of Hard Rubber Composition Material

Hoenes, H. S., 2,686,153, Apparatus for



ELECTROLYTIC MANGANESE DIOXIDE

The Tennessee Corporation is pleased to announce the limited production of **Electrolytic Manganese Dioxide**. This TC product, the result of more than four years collaborative research with the **US Army Signal Corps**, is now available in semi-work quantities. Possessing greater stability, exceptional purity, higher capacity and uniformity, Tennessee's **Electrolytic Manganese Dioxide** may well be the answer to your dry cell battery problems.

Direct inquiries to
our research laboratories.

TENNESSEE
RESEARCH



CORPORATION
LABORATORIES

College Park, Ga.

MANUSCRIPTS AND ABSTRACTS FOR SPRING MEETING

Manuscripts are now being received for the Spring Meeting of the Society, to be held at the Sheraton-Gibson Hotel in Cincinnati, May 1, 2, 3, 4, and 5, 1955. Subjects to be covered at the technical sessions probably will be Electric Insulation, Electronics, Electrothermics and Metallurgy, Industrial Electrolytics, and Theoretical Electrochemistry.

To be considered for this meeting, triplicate copies of manuscripts or abstracts (not to exceed 75 words in length) must be received at Society headquarters, 216 West 102nd Street, New York 25, N. Y., *not later than January 15, 1955.*

Generating Hydrogen and Oxygen
Jones, S., 2,686,157, Fluorescent Coat-
ing Composition and Process

Jones, S., 2,686,158, Fluorescent Coat-
ing Composition and Process Em-
ploying Boric Acid

Cargill, A. B., 2,686,211, Combustion
Furnace

Horn, F. H., and Neubauer, R. L.,
2,686,212, Electric Heating Appara-
tus

Smyth, J. R., 2,686,213, Battery Plate
and Method of Making Same

Arbogast, R. D., 2,686,214, Primary
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- Southern, R. L., 2,686,825, Furnace Structure
 Paine, H. A., 2,686,826, Furnace Structure
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 Friedman, H., 2,688,097, Nitric Oxide Counter

LITERATURE FROM INDUSTRY

"NORTON REFRACTORIES FOR THE CERAMIC INDUSTRY." New 28-page booklet describes Norton Refractories, their properties and their advantages to specific applications. In addition, it contains engineering tables and other data used in connection with the employment of refractories in the ceramic in-

dustry. This information should be helpful to plant managers, superintendents, design engineers, and kiln foremen. Norton Co. P-247

FISHER'S NEW CATALOGUE. The most complete listing of laboratory chemicals anywhere is found in the new Fisher Chemical Index, the all-inclusive chemicals Blue Book. Fact-filled, cross-referenced, the catalogue lists all needed information on 7244 chemicals and reagents available at Fisher. Copies on request. Fisher Scientific Co. P-248

ELECTROPLATING PROCESSES. 4-page, 2-color bulletin describes and lists key characteristics of 16 electroplating processes. These include 7 nickel plating, 3 zinc, 1 cadmium, 1 copper with and without periodic reverse current, 2 silver, 1 lead, and 1 bright ternary alloy plating process. Also included is a list of 10 services available to H-VW-M customers. Hanson-Van Winkle-Munning Co. P-249

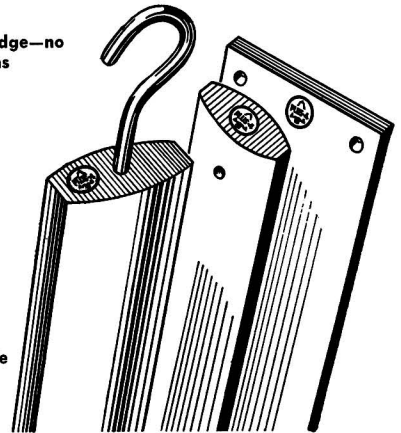
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selection of molybdenum products for applications in the chemical process industries. It describes briefly the commercially available products, their manufacture, and their principal uses. It also lists the molybdenum chemicals available as analytical reagents and laboratory chemicals. In addition, the bulletin mentions sources of further information on the chemical properties and applications of molybdenum. Climax Molybdenum Co. P-250

"INSTRUMENTATION." Among the industrial developments reported in the current issue of "Instrumentation" are production techniques in the processing of the polio-fighting serum gamma globulin and the design of a weighing device so sensitive it can measure and record the difference in weight between a broad and a narrow pencil line. Also included are articles on boiler tube measurement, a report on the use of a new servo-analyzer, electronic burnout protection for a 60-ft rotary press and controls to regulate start-up procedures in an open hearth furnace. Minneapolis-Honeywell Regulator Co. P-251

BURRELL TUBE FURNACES. Bulletin gives complete data, including description of models and sizes, catalogue numbers, dimensions, specifications, ordering data and prices, of the Burrell high temperature electric tube furnaces for laboratories. Separate charts list heating elements required. Burrell "H" Models, new this year, are a new concept in tube furnace design. Faster heating, cooler operation, and greater flexibility are pointed up as features. Burrell Corp. P-252

MECHANICAL FINISHING. 4-page, 2-color bulletin describes products and equipment used for mechanical metal finishing. It lists H-VW-M's line of standard buffs, compositions, sisal buffs, brushes, polishing wheels, polishing and buffing lathes, and miscellaneous equipment and accessories. Literature references are included for all products and equipment. The bulletin thus serves as

a handy index on the entire line of H-VW-M mechanical metal finishing products. Hanson-Van Winkle-Munning Co. P-253

NEW PRODUCTS

HEAVY DUTY ELECTROCLEANER. A new, heavy duty electrocleaner known as Pennsalt Cleaner K-8 has been introduced. Recommended for use on steel and copper, K-8 provides excellent detergency properties with unusual ability to remove mill oil and smut from steel prior to electroplating. The cleaner is a granular, anhydrous product containing 100% active ingredients which resist neutralization by acid soils, and provides excellent electrical conductivity. It is resistant to the effects of hard water and is free rinsing. Pennsylvania Salt Manufacturing Co. N-121

STATIONARY BATTERIES. Stationary batteries specifically designed for use in switchgear, control, and auxiliary power applications have been announced. They are made in two complete lines, PlastiCell and PlastiCal. Both lines have extra-thick positive plates with triple insulation suspended from ledges molded into the jar, thus allowing normal plate growth without strain on the cover. In addition, both feature: Plastite Post Seals which eliminate acid creepage, Safetee Vents which greatly reduce explosion hazards, and high-low level lines for easy visual checking of the electrolyte level. C & D Batteries, Inc. N-122

3-SPEED STIRRER. New 3-Speed Stirrer offers laboratories the "Hollow Spindle" and continuous, light duty operation at 500, 750, or 1000 rpm. The 1/50-hp split-phase, induction motor by Bodine develops 4 inch-pounds of torque. Stirrer is driven by V-belt on 3-step pulleys. Motor and stirrer are mounted on a 2-piece frame adjustable to maintain V-belt tension. The custom stirrer clamp allows adjustment in three planes. Eberbach Corp. N-123

ALKALINE RUST REMOVER. Nonelectrolytic alkaline derusting compound known as Alka-Deox 114 is stated to be a free-flowing powder that is used in a concentration from 1 to 3 lb/gal of water. Due to its alkaline nature there is no attack upon the base steel, leaving it clean and bright, and, because of its

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high alkalinity, paints, organic coatings, and other surface contaminants are removed together with rust. Due to the lack of necessity to use electric current, the product is stated to be ideal for bulk derusting of steel and cast and malleable iron. Bulletin on request. Enthone, Inc. N-124

TELEDYNE PRESSURE TRANSMITTER. Recently developed Teledyne Bonded Strain Gage Pressure Transmitter provides a new high standard of accurate and dependable transmission of pressure information from a remote or hazardous location to a central control room which may be several thousand feet distant. Used in combination with suitable self-balancing potentiometer type recorders, controllers, and valve systems, the Teledyne will control pressure of chemical and similar processes with a high degree of accuracy and reliability. Taber Instrument Corp. N-125

IRIDITE FINISHES. Five protective coatings for zinc, silver, copper, and aluminum have been added to the Iridite line of corrosion resistant finishes for nonferrous metals. The new Iridites are: #4-73 and #4-75 (Cast-Zinc-Brite), #18-P (Silver-Kote), #17-P (Cupreous-Kote), and #14-2 (Al-Coat). Like all Iridite finishes for nonferrous metals, the five new products are applied by a simple chemical dip, without electrolysis and without the need for special equipment or specially trained personnel. Their development increases the number of Iridite finishes to a total of 25. Full information on request. Allied Research Products, Inc. N-126

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.

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Manuscripts submitted for publication should be in triplicate to expedite review. They should be typewritten, double-spaced, with $2\frac{1}{2}$ –4 cm (1 – $1\frac{1}{2}$ in.) margins.

Title should be brief, followed by the author's name and his business or university connection.

Abstract of about 100 words should state the scope of the paper and give a brief summary of results.

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Drawings will be reduced to column width, 8 cm ($3\frac{1}{8}$ in.), and after reduction should have lettering at least 0.15 cm ($\frac{1}{16}$ in.) high. Original drawings in India ink on tracing cloth or white paper are preferred. Curves may be drawn on coordinate paper only if the paper is ruled in blue. All lettering must be of lettering-guide quality. See sample drawing on reverse page.

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General—Figures should be used only when necessary. Omit drawings or photographs of familiar equipment. Figures from other publications are to be used only when the publication is not readily available, and should always be accompanied with written permission for reprinting.

REFERENCES

Literature and patent references should be listed at the end of the paper on a separate sheet, in the order in which they are cited. They should be given in the style adopted by *Chemical Abstracts*. For example:

R. Freas, *Trans. Electrochem. Soc.*, **40**, 109 (1921).

H. T. S. Britton, "Hydrogen Ions," Vol. **1**, p. 309, D. Van Nostrand Co., New York (1943).

H. F. Weiss (To Wood Conversion Co.), U. S. Pat. 1,695,445, Dec. 18, 1928.

Metric units should be used throughout but, where desirable, English units may be given in parentheses.

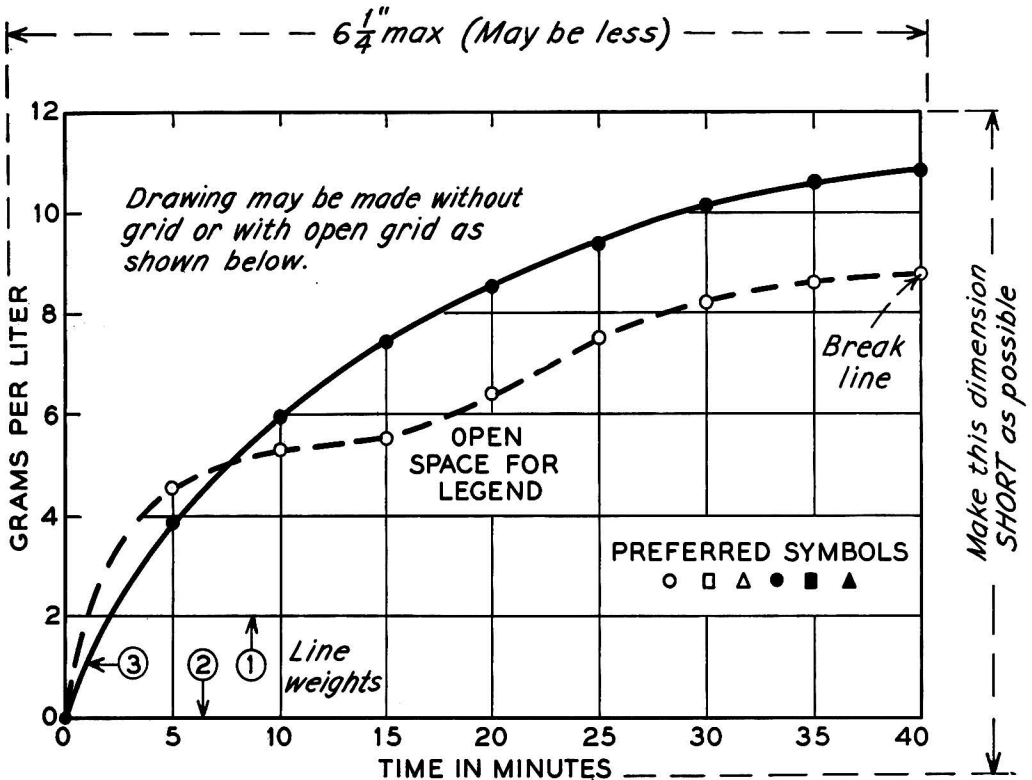
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Authors should be as brief as is consistent with clarity, and must omit all material which can be regarded as familiar to specialists in the particular field.

The use of proprietary names, trade-marks, and trade names should be avoided if possible. If used, these should be capitalized so that the owner's legal rights are not jeopardized.



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