[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Study of the Polarographic Behavior of Dropping Amalgam Electrodes[1]

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Introduction

This paper presents a detailed experimental study of the main aspects of the polarography of dilute amalgam anodes. The possibility of developing a new method of chemical analysis, particularly of alloys, based on dropping amalgam electrodes as first suggested by Heyrovsky and Kalousek[2] led to a quantitative study of the polarographic behavior of simple and composite[3] amalgams of zinc, cadmium, thallium, lead and copper. Our quantitative study was made possible through the use of a special apparatus and technique whereby amalgams of known concentration were prepared and dropped through a capillary in the virtual absence of air. In general, it appears that the anodic dissolution of metals from mercury is not as simple a process as has heretofore been supposed.

The first reported study on current–voltage curves obtained using dropping amalgam electrodes in place of the usual dropping mercury electrode is that of Lingane[4] who dropped an approximately 0.01% cadmium amalgam into an air-free solution of 0.1 *M* potassium chloride which was 0.04 *M* with respect to cadmium sulfate. The combined cathodic–anodic wave which Lingane obtained had a sharp anodic maximum which was suppressed by the addition of sodium methyl red.

A more extensive study on dropping amalgam electrodes was made by Heyrovsky and Kalousek.[2] These investigators deduced an equation for the current–voltage curve obtained when a dilute amalgam is used in the dropping electrode instead of mercury and studied the polarographic behavior of amalgams of copper, lead, cadmium and zinc in concentrations not exceeding 0.005%. Although Heyrovsky and Kalousek state that the waves obtained were proportional to concentration, no quantitative data are presented to substantiate the statement.

Heyrovsky and Forejt[5] conducted an interesting investigation on the oscillographic potential–time curves with an a.c. of 50 cycles for 0.003% amalgams of copper, bismuth, lead, thallium and cadmium. The amalgams were dropped into a number of supporting electrolytes including 1 *N* nitric acid, hydrochloric acid, sulfuric acid, potassium chloride, potassium iodide, potassium carbonate, lithium hydroxide, potassium hydroxide, potassium cyanide, ammonium thiocyanate and 10% sodium potassium tartrate. It was found that for the most part the potential–time curves and the spectra of the amalgams agreed with the oscillograms obtained when the cations were in solution and the dropping mercury electrode was used. Heyrovsky and Forejt concluded that, since the reproducibility of the anodic oscillograms was the same as that for the cathodic, the technique could be used for the quantitative analysis of amalgams.

Reboul and Bon[6] also used the cathode ray oscillograph to study dropping amalgam electrodes. They investigated the variations in the instantaneous current, measured during the formation of the drop, as a function of time. It was found that if mercury is replaced by an amalgam of a base metal such as zinc, lead or tin, certain changes occur in the current–time curve. Reboul and Bon attributed these changes to the oxidizability of the impure mercury. If noble metals such as gold or silver are dissolved in mercury, the curve obtained with these amalgams is the same as that for pure mercury.

Although no details of their experiments are given, Stackelberg and Freyhold[7] studied current–voltage curves with dropping amalgam electrodes and claimed to have found anodic diffusion currents which were of the order of magnitude to be expected if D_a, the diffusion coefficient of the metal atoms in mercury, was substituted for D_s, the diffusion coefficient of the metal ions in solution, in the Ilkovic equation.

Experimental

Apparatus and Materials.—The major portion of this investigation was carried out using the Fisher Elecdropode. The Elecdropode galvanometer was calibrated according to the procedure given by Kolthoff and Lingane[8] and was found to have a value of 7.92×10^{-3} microampere per millimeter at a sensitivity of one. The Elecdropode potential scale was calibrated by Karl Roberts of this Laboratory by measuring the nominal values of the potential with an accurate potentiometer. A Leeds and Northrup student-type potentiometer was used for the measurements of the amalgam pool *vs.* saturated calomel electrode potentials.

Through the courtesy of the Leeds and Northrup Co., Phila., Pa., a research model of the Leeds and Northrup Electro-Chemograph Type E was also used for recording the polarograms. In the measurement of half-wave potentials the corrections for lag at the various dampings worked out by C. E. Bricker of this Laboratory were applied.

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(1) Abstracted from a thesis submitted by W. Charles Cooper in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Princeton University, December, 1948.

(2) J. Heyrovsky and M. Kalousek, *Collection Czechoslov. Chem. Commun.*, **11**, 464 (1939).

(3) In this paper amalgams that contains only one metal added to mercury are referred to as simple and those with two or more metals to mercury are called composite.

(4) J. J. Lingane, THIS JOURNAL, **61**, 976 (1939).

(5) J. Heyrovsky and J. Forejt, *Z. physik. Chem.*, **193**, 77 (1943).

(6) G. Reboul and F. Bon, *Compt. rend.*, **224**, 1263 (1947).

(7) M. v. Stackelberg and H. v. Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

In this investigation the usual polarographic cell assembly could not be used for several reasons. Since a quantitative study of the behavior of dropping amalgam electrodes was the principal object of the research, it was necessary to prevent loss of base metal in the amalgams through air oxidation. Heyrovsky and Kalousek[2] in their studies on dropping amalgam electrodes failed to exclude air from their apparatus and reported that the same amalgams gave different wave heights at different intervals of time and that a considerable decrease in anodic current was observed after shaking the amalgam. The writers were unable to obtain any correlation between wave height and concentration for zinc amalgams when they prepared the amalgams by mercury cathode electrolysis and transferred the same to the ordinary dropping apparatus. The apparatus which was finally devised is illustrated in Fig. 1 and is a modification of that described by Cooper and Wright.[9] Actually it is a unitized mercury cathode cell–polarographic dropping electrode. Such an apparatus makes possible the convenient preparation of amalgams and the dropping of these amalgams through a capillary in the virtual absence of air. By passing a fairly vigorous stream of purified nitrogen through the apparatus for 30 minutes prior to draining the amalgam from the cell into the dropping apparatus, it was possible to sweep out nearly all the air. Since in this work it was necessary to disassemble and clean the apparatus after each run, it was desirable to have a set-up which could be conveniently put through this procedure. The apparatus used meets this requirement since it consists of four pieces easily cleaned and joined by ground-glass connections.

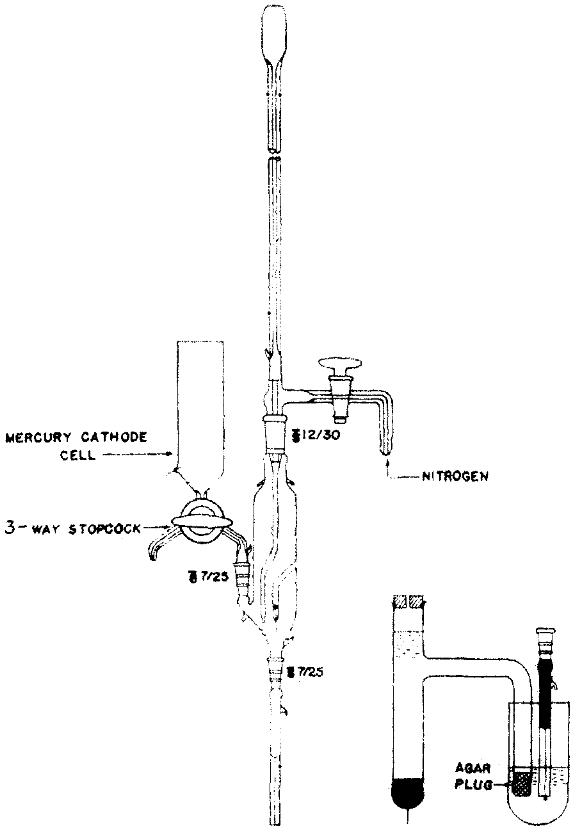

Fig. 1.—Apparatus for preparation and dropping of amalgams. 1A. Polarographic cell with zinc amalgam reference electrode. The tubes for the passage of purified nitrogen through and above the solution are not shown.

The capillary consists of 5.5 cm. of Corning marine barometer tubing connected to a soft-glass ground-glass joint. As such it was easily disconnected and cleaned. The ground-glass parts of the apparatus were adequately held in place with the aid of stout rubber bands held by the glass lugs shown in Fig. 1.

A number of amalgams were prepared by electrolysis. Various weighed portions of these amalgams were analyzed by extracting the active metal from the mercury with acid. After the proper adjustment of conditions, the metal was determined polarographically. In this manner it was proved that homogeneous dilute amalgams of known composition could be prepared by the electrolytic technique.

Standard solutions of each of the metal ions whose amalgam was being studied were prepared from C. P. reagents.

The mercury used in this research was purified by aeration, filtration, washing with nitric acid then water, drying, and two distillations *in vacuo*.

For the large unpolarizable electrode a pool of the amalgam was used in much of this work. The disadvantages of this electrode caused the authors to adopt finally a zinc amalgam electrode consisting of a 2% zinc amalgam in 0.1 N zinc sulfate. This electrode proved to be satisfactory. The correction for the iR drop in the cell occasioned by the use of this electrode was always applied. The electrode vessel, used for both the saturated calomel electrode and the zinc amalgam electrode, and shown in Fig. 1A conformed to the design suggested by Norton.[10]

The mass of amalgam falling per second was always determined in the medium in question and at the potential at which the current had a limiting value. The drop time was always determined under these same conditions. The inverted capillary tube of Lingane and Kolthoff[11] was used to collect the drops in the determination of m.

The nitrogen employed was purified according to the procedure of Meites and Meites.[12]

The temperature was maintained at 25.0 ± 0.5° in all experiments.

All wave heights were measured and the correction made for the residual current by the extrapolation method described by Kolthoff and Lingane.[8]

Throughout this work the usual criterion was used to determine the presence or absence of maxima, *viz.*, an abnormal rise in the current in the potential region where the limiting current is ordinarily being established was taken to indicate a maximum.

General Procedure for the Preparation and Dropping of Amalgams.—The apparatus shown in Fig. 1 was thoroughly cleaned and dried, then assembled. The capillary was not attached until 30 minutes before dropping the amalgam because it was feared that it could be fouled in some way if allowed to stand in air for a long period. Approximately 140 g. of pure mercury were accurately weighed out and put into the mercury cathode cell. Care was taken to ensure the absence of any air locks in the lower region of the cell. Approximately 50 ml. of a very dilute acid solution containing a known amount of the standard solution of the metal whose amalgam it was desired to prepare was then added to the electrolysis cell. The amount of standard solution used was usually such as to give an amalgam not more concentrated than 0.005%. The electrolysis was commenced, a current of approximately 15 milliamp. being used, and was allowed to proceed for a period of 8 hours, generally overnight. Toward the conclusion of the electrolysis period, the capillary was attached and a fairly vigorous stream of purified nitrogen was passed through the apparatus to sweep out the air. The amalgam was then drained into the dropping apparatus and raised under pressure of nitrogen to a height in the stand-tube at which it was known that the amalgam would issue satisfactorily from the capillary. With the amalgam dropping, the anodic waves for the dissolution of the metal in the amalgam in various media were taken

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(9) W. C. Cooper and M. M. Wright, *Anal. Chem.*, **22**, 1213 (1950).

(10) D. R. Norton, Ph.D. Thesis, Princeton University, 1948.

(11) J. J. Lingane and I. M. Kolthoff, This Journal, **61**, 825 (1939).

(12) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

in the usual way, in this case either the Elecdropode or the research model of the Leeds and Northrup Electro-Chemograph Type E being employed. The voltage was applied between the dropping electrode and the zinc amalgam reference electrode. The mass of amalgam falling per second and the drop time were determined in the manner already described. In order that all measurements might be referred to the saturated calomel electrode, the potential of the zinc amalgam electrode *vs.* the saturated calomel electrode was always determined in the supporting electrolyte in question.

Results and Discussion

Cadmium Amalgams.—The half-wave potentials (volts *vs.* saturated calomel electrode) of the anodic waves are compared with those reported for the cathodic waves in Table I.

TABLE I

ANODIC AND CATHODIC HALF-WAVE POTENTIALS FOR CADMIUM

Supporting electrolyte	$E_{1/2}$ *vs.* S. C. E. (anodic)	$E_{1/2}$ *vs.* S. C. E. (cathodic)
0.1 *M* KCl	−0.60	−0.599
0.1 *M* KNO_3	−0.58	−0.578
1 *M* NH_3–1 *M* NH_4Cl	−0.79	−0.81
1 *M* KCN	−1.06	−1.18
1 *M* KI	−0.74	−0.74
0.5 *M* NaK tartrate	−0.64	−0.64

The agreement between the half-wave potentials indicates that the reduction of cadmium is reversible in all media except 1 *M* potassium cyanide. Although Pines[13a] and Demassieux and Heyrovsky[13b] reported the reduction of cadmium in 1 *M* potassium cyanide to be reversible, Kolthoff and Lingane[7] found that the slope of the cathodic wave was considerably smaller than it would be if the reduction were perfectly reversible and reported a half-wave potential of −1.18 volts. The value for the half-wave potential calculated using Euler's value for the dissociation constant of $Cd(CN)_4^=$,[14] 1.4×10^{-17} and the half-wave potential of the simple cadmium ion in 1 *M* potassium nitrate (−0.586 volt) is −1.08 volts. The half-wave potential for the anodic wave, −1.06 volts, agrees well with this value. Hence the reduction of cadmium in 1 *M* potassium cyanide is not perfectly reversible.

Waves for cadmium amalgam in 0.1 *M* potassium chloride and 1 *M* ammonia–1 *M* ammonium chloride are shown in Fig. 2. Equally well-defined waves were obtained in the other supporting electrolytes mentioned in this discussion with the exception of 1 *M* potassium cyanide. In this medium the wave had a slope indicative of the irreversible behavior discussed above.

Lead Amalgams.—Table II is a comparison of the half-wave potentials *vs.* saturated calomel electrode for the anodic and cathodic waves of lead.

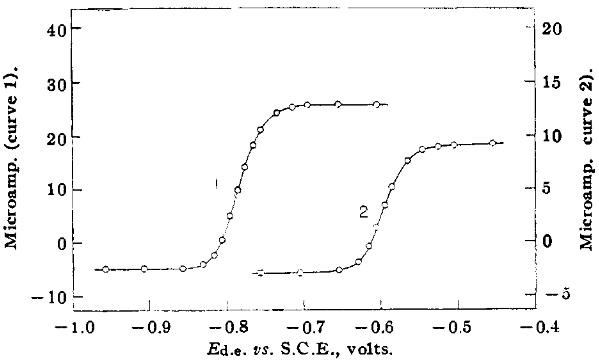

Fig. 2.—Curve 1, polarogram of 0.00287% cadmium amalgam in 1 *M* ammonia–1 *M* ammonium chloride 0.01% in gelatin and 0.81 millimolar in cadmium ions; curve 2, polarogram of 0.00109% cadmium amalgam in 0.1 *M* potassium chloride 0.01% in gelatin and 0.534 millimolar in cadmium ions.

TABLE II

ANODIC AND CATHODIC HALF-WAVE POTENTIALS FOR LEAD

Supporting electrolyte	$E_{1/2}$ *vs.* S. C. E. (anodic)	$E_{1/2}$ *vs.* S. C. E. (cathodic)
0.1 *M* KCl	−0.39	−0.396
0.1 *M* HCl	− .39	− .396
0.5 *M* NaK tartrate	− .49	− .50
1 *M* NaOH	− .76	− .755

The agreement between the half-wave potentials is satisfactory, indicating that the reduction of lead in these media is reversible.

Any wave that might have appeared for the dissolution of lead amalgam in 1 *M* potassium cyanide was entirely blanked out by the large wave for the anodic solution of mercury.

$$Hg + 2CN^- \longrightarrow Hg(CN)_2 + 2e$$

Copper Amalgam.—Well-defined waves were obtained in 0.1 *M* potassium nitrate and 0.5 *M* sodium potassium tartrate in the presence of gelatin. In 1 *M* ammonia–1 *M* ammonium chloride the oxidation was stepwise, two waves being obtained—just the reverse of the reduction of copper ions in this supporting electrolyte. However, in 0.1 *M* potassium thiocyanate only one wave was obtained, the height of which indicated oxidation of the copper to the cuprous state. The second wave was blanked out by the anodic solution of mercury

$$Hg + 2CNS^- \longrightarrow Hg(CNS)_2 + 2e$$

A further discussion of the behavior of copper amalgams together with half-wave potential data will be presented in a later paper.

Thallium Amalgams.—Thallium amalgams gave well-defined waves in 0.1 *M* potassium chloride and 0.1 *M* potassium nitrate in the presence of gelatin. The half-wave potentials *vs.* saturated calomel electrode of the anodic waves, −0.46 volt in 0.1 *M* potassium chloride and −0.46 volt in 0.1 *M* potassium nitrate, are in agreement with the value for the reverse process in these media, *viz.*, −0.460 volt. The wave for

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(13) (a) I. Pines, *Collection Czechoslov. Chem. Commun.*, **1**, 387 (1929); (b) M. Demassieux and J. Heyrovsky, *Bull. soc. chim.*, **45**, 30 (1929).

(14) H. Euler, *Ber.*, **36**, 3400 (1903).

thallium amalgam in 1 *M* potassium cyanide was completely obscured by the large wave for the anodic solution of mercury.

Zinc Amalgams.—Well-defined waves were obtained in 0.1 *M* hydrochloric acid, 1 *M* potassium cyanide, 1 *M* ammonia-1 *M* ammonium chloride and 1 *M* sodium hydroxide in the presence of gelatin.

The fact that a wave is obtained in 1 *M* potassium cyanide is of interest since no reduction has been found to occur in the same medium. The absence of a cathodic wave in fairly concentrated cyanide solution has been interpreted by Pines[15] as due to the formation of $Zn(CN)_6^{-4}$, the reduction potential of which is apparently more negative than that of potassium ion. The half-wave potential of the anodic wave, −1.1 volts, corresponds most closely to that for the wave which Pines attributed to the $Zn(CN)_4^{=}$ ion. Pines found a half-wave potential of −1.2 volts. Although a direct comparison of these half-wave potentials is not possible since Pines used as supporting electrolyte 0.001 to 0.01 *M* solutions of potassium cyanide, it is certain that when zinc is oxidized in 1 *M* potassium cyanide a complex ion is produced and that $Zn(CN)_4^{=}$ is a likely species.

The waves for zinc amalgams in 0.1 *M* potassium chloride and 0.1 *M* potassium thiocyanate were found to have pronounced maxima on which gelatin had no effect. These maxima persisted in 0.1 *M* potassium chloride buffered at *p*H 4 with an acetate buffer but disappeared when the same medium was buffered at *p*H 2 with hydrochloric acid buffer.

Table III is a comparison of the half-wave potentials *versus* saturated calomel electrode for the anodic and cathodic waves.

TABLE III

ANODIC AND CATHODIC HALF-WAVE POTENTIALS FOR ZINC

Supporting electrolyte	$E_{1/2}$ *vs.* S. C. E. (anodic)	$E_{1/2}$ *vs.* S. C. E. (cathodic)
0.1 *M* KCl buffered *p*H 2	−1.00	(−0.995)[a]
0.1 *M* HCl	−0.98	
1 *M* KCN	−1.1	No redn.
1 *M* NH_3-1 *M* NH_4Cl	−1.1	−1.36
1 *M* NaOH	−1.3	−1.56

[a] 0.1 *M* KCl.

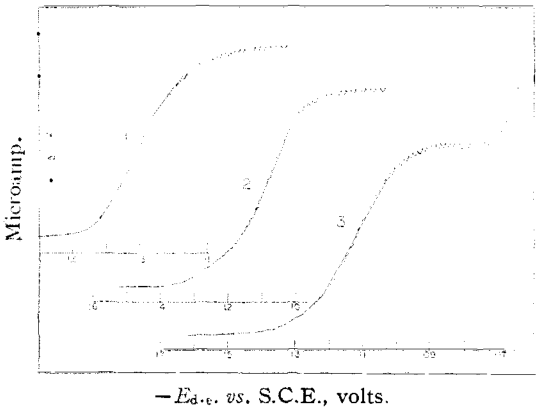

Fig. 3.—Polarograms of 0.00048% zinc amalgam: curve 1, in 1 *M* sodium hydroxide 0.01% in gelatin; curve 2, in 1 *M* ammonia-1 *M* ammonium chloride 0.01% in gelatin; curve 3, in 1 *M* potassium cyanide 0.01% in gelatin.

It would appear that the reduction of zinc in ammoniacal and sodium hydroxide solutions is not a reversible process. It is significant that Kolthoff and Lingane[4] found that the reduction of zinc in sodium hydroxide solution is not perfectly reversible, the slope of their wave being somewhat smaller than the theoretical value for $n = 2$. In oscillographic studies Heyrovsky[16] found zinc to be deposited irreversibly in neutral, acid, ammoniacal and alkaline solutions. Thus in a 1 *N* ammonium sulfate-1 *N* ammonia solution 0.002 *N* in zinc, Heyrovsky found the cathodic potential to be at −1.46 volts and the anodic at −0.87 volt. This shift in potential agrees not unsatisfactorily with that observed in this study. Figure 3 shows the anodic waves for zinc in 1 *M* potassium cyanide, 1 *M* sodium hydroxide and 1 *M* ammonia-1 *M* ammonium chloride.

Composite Amalgams.—Composite or multicomponent amalgams comprising the metals zinc, cadmium, lead, thallium and copper were studied in the following supporting electrolytes: 0.1 *M* potassium nitrate, 0.1 *M* potassium chloride, 0.1 *M* hydrochloric acid, 0.5 *M* sodium potassium tartrate, 0.1 *M* potassium thiocyanate, 1 *M* potassium cyanide, pyridine-pyridinium chloride, 1 *M* ammonia-1 *M* ammonium chloride and 1 *M* sodium hydroxide. The behavior here was for the most part in accordance with the observations which had been made on simple amalgams. However, the maxima which were encountered with zinc amalgams in 0.1 *M* potassium chloride and 0.1 *M* potassium thiocyanate were not found when zinc was accompanied in the mercury by one or more of the other base metals. The well-defined nature of the waves for a composite amalgam of zinc, cadmium, lead and copper in 0.1 *M* potassium nitrate is shown in Fig. 4.

Like 0.1 *M* potassium nitrate, 0.5 *M* sodium potassium tartrate proved to be a very satisfactory medium for the study of composite amalgams of combinations of the five metals mentioned.

In the study of an amalgam of zinc, cadmium, lead and copper in 1 *M* potassium cyanide the waves for zinc and cadmium coalesced, the half-wave potentials of these metals in this solution being so close together. The height of the single wave agreed with the combined height of the zinc and cadmium waves for this amalgam in other media. Due to the anodic solution of mercury no waves were obtained for lead and copper in 1 *M* potassium cyanide.

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(15) I. Pines, *Collection Czechoslov. Chem. Commun.*, **1**, 429 (1929).

(16) J. Heyrovsky, *Discussions Faraday Soc.*, **1**, 212 (1947).

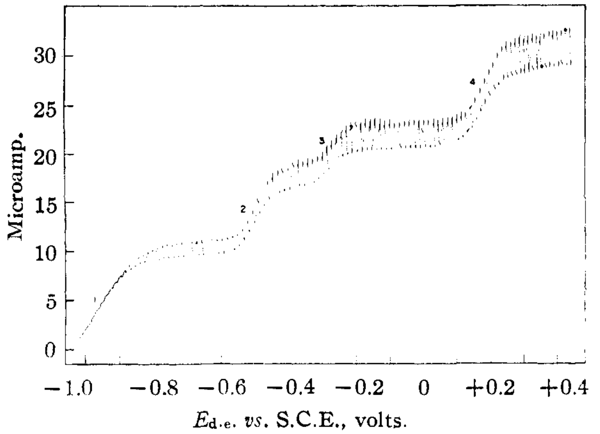

Fig. 4.—Polarogram of 0.00307% composite amalgam of zinc, cadmium, lead and copper in 0.1 *M* potassium nitrate 0.01% in gelatin. The successive waves 1, 2, 3, 4 are for zinc, cadmium, lead and copper, respectively.

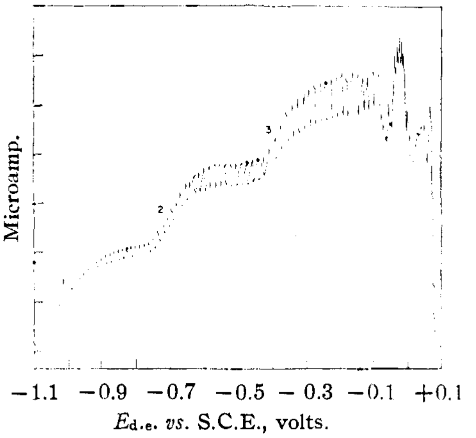

Fig. 5.—Polarogram of 0.00307% composite amalgam of zinc, cadmium, lead and copper in 1 *M* ammonia–1 *M* ammonium chloride 0.01% in gelatin. The successive waves 1, 2, 3 are for zinc, cadmium and lead, respectively.

In ammoniacal medium, for an amalgam of zinc, cadmium, lead and copper, well-defined zinc and cadmium waves resulted. However, the wave for lead and the first wave for copper coalesced. As might be expected and as is shown in Fig. 5 the formation of slightly soluble hydrous lead oxide affected the drop time of the amalgam eventually stopping the dropping altogether. As soon as the potential was reduced below that for the oxidation of lead the amalgam dropped regularly again.

The half-wave potentials for the metals in composite amalgams are not in agreement with those for the simple amalgams. The fact that the potentials have shifted to less positive values is possibly indicative of complexation or intermetallic compound formation in the mercury[17–20] although this formation has not been established for as dilute amalgams as were employed in this study. A more detailed investigation of the preliminary observations is being undertaken.

Maxima in the Polarographic Waves of Amalgams.—In the study of dropping amalgam electrodes anodic maxima were observed which had many of the characteristics of those obtained in cathodic polarography. Some of these maxima were sharp, others rounded and like cathodic maxima their size depended on the concentration of the oxidizable species. The concentration of the reducible species was also a determining factor. Thus a 0.00109% cadmium amalgam gave no maximum in 0.1 *M* potassium chloride whereas the same amalgam produced a maximum in 0.1 *M* potassium chloride which was 0.178 millimolar in cadmium ions.

The cathodic maxima occurring at dropping amalgam electrodes like those at the dropping mercury electrode were found to depend on the concentration of the reducible ions. However, in only three instances were cathodic maxima observed when both oxidizable and reducible species were present: (1) 0.00227% lead amalgam in 0.1 *M* potassium chloride 0.74 millimolar in lead ions; (2) 0.00227% lead amalgam in 0.1 *M* hydrochloric acid 0.44 millimolar in lead ions; (3) 0.00027% copper amalgam in 0.5 *M* sodium potassium tartrate 3.05 millimolar in copper ions. In no case were both cathodic and anodic maxima observed for a combined cathodic–anodic wave.

For some amalgams in certain media no anodic maxima were observed. Thus cadmium amalgam produced no maximum in 1 *M* potassium cyanide, lead amalgam none in 0.1 *M* potassium chloride and 0.1 *M* hydrochloric acid, copper amalgam none in 0.5 *M* sodium potassium tartrate and 0.1 *M* potassium thiocyanate and thallium amalgam none in 0.1 *M* potassium chloride. In view of the effect which the metal in the amalgam and the solution have on the electrocapillary maximum it is conceivable that in the case of cadmium amalgam in 1 *M* potassium cyanide no maximum was obtained because the electrocapillary had been shifted so that the electrocapillary zero was very close to the oxidation potential of cadmium in cyanide medium.

The fact that the anodic and cathodic maxima with the exception of the anomalous zinc maxima previously discussed, can be suppressed by the usual maximum suppressors indicates that the excessive currents are due to phenomena taking place on the solution side of the amalgam–solution interface. However, none of the existing theories on maxima can explain satisfactorily all the observations which have been made. Of the theories which have been proposed that of Antweiler[21] appears to be the most satisfactory.

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[17] A. S. Russell, *Nature*, **125**, 89 (1930).

[18] A. S. Russell, P. V. F. Cazalet and N. M. Irvin, *J. Chem. Soc.*, **135**, 841 (1942).

[19] Russell, *et al.*, *ibid.*, **135**, 852 (1932).

[20] A. S. Russell and H. A. M. Lyons, *ibid.*, **135**, 857 (1932).

[21] H. J. Antweiler, *Z. Elektrochem.*, **43**, 596 (1937); **44**, 831, 888 (1938).

Anodic maxima given by cadmium and copper amalgams are shown in Figs. 6 and 7.

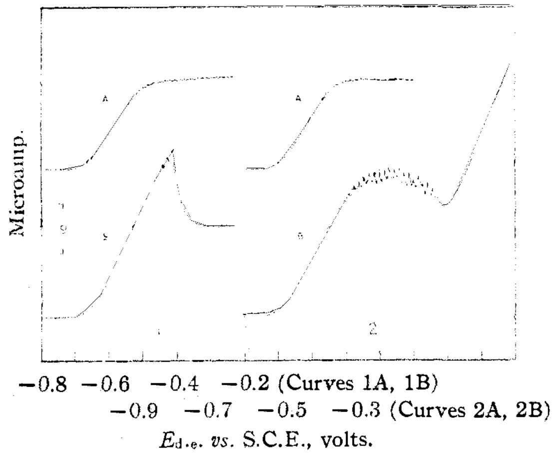

Fig. 6.—1. Polarograms of 0.00207% cadmium amalgam in 0.1 *M* potassium chloride with (A) and without (B) gelatin. 2. Polarograms of 0.00207% cadmium amalgam in 1 *M* potassium iodide with (A) and without (B) gelatin.

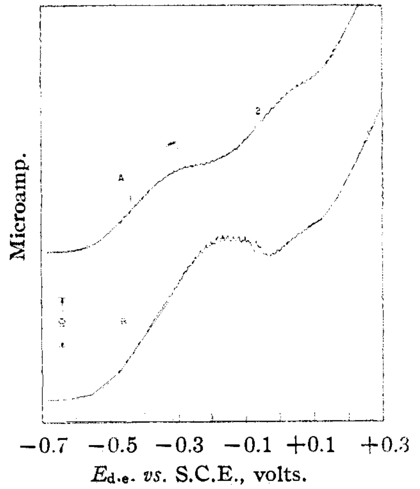

Fig. 7.—Polarograms of 0.00291% copper amalgam in 1 *M* ammonia–1 *M* ammonium chloride with (A) and without (B) gelatin: 1, Cu^0 to Cu^I wave; 2, Cu^I to Cu^{II} wave.

Diffusion Current.—Although the Ilkovic equation is concerned with the current produced by the diffusion of ions in the solution to the dropping mercury electrode, an equation of similar form (4) is applicable to the anodic current produced by the diffusion of metal atoms from the interior to the surface of a growing amalgam drop. The fundamental differential equation for diffusion to the dropping mercury electrode is[22]

$$\frac{\partial c}{\partial t} = \frac{D_a r^4}{\rho^5}\left[\rho\frac{\partial^2 c}{\partial \rho^2} + 2\frac{(\rho^3 - \partial t)}{(\rho^3 + \gamma t)}\frac{\partial c}{\partial \rho}\right] \qquad (1)$$

It can be shown that the corresponding equation for the dropping amalgam electrode in the case of which the diffusion is taking place inside the drop is

$$\frac{\partial c}{\partial t} = \frac{D_a r^4}{\rho^5}\left[-\rho\frac{\partial^2 c}{\partial \rho^2} + 2\frac{(\rho^3 + \gamma t)}{(\gamma t - \rho^3)}\frac{\partial c}{\partial \rho}\right] \qquad (2)$$

For the region very close to the surface of the dropping electrode equation 2 becomes

$$\frac{\partial c}{\partial t} = \frac{-D_a(\gamma t)^{4/3}}{\rho^5}\left[\rho\frac{\partial^2 c}{\partial \rho^2} - \frac{2\partial c}{\partial \rho}\right] \qquad (3)$$

This equation is identical with that for the dropping mercury electrode except for sign and the diffusion coefficient. Following MacGillavry and Rideal's derivation[23] from this point, we finally arrive at the following equation for the average diffusion current

$$i_d = -knD^{1/2}Cm^{2/3}t^{1/6} \quad {}^{24,25} \qquad (4)$$

where *D* is the diffusion coefficient of the metal in mercury.

According to equation (4) an accurate knowledge of diffusion coefficients should enable us to calculate the diffusion current, providing, of course, we know *n*, *m* and *t*. It is unfortunate that the literature contains only one diffusion coefficient which can be applied with any confidence to the polarographic study of dropping amalgam electrodes. This is the diffusion coefficient for cadmium.[26,27] Although Weischedel[26] has shown that the diffusion coefficient for zinc is a function of concentration, it is to be expected that this relation becomes less valid as the amalgam concentration decreases. In accordance with this assumption, Weischedel's largest value for *D* (1.67×10^{-5} cm.^{2} sec.$^{-1}$—concentration of amalgam 0.235%) was employed for the calculation of diffusion currents.

The data for cadmium amalgams are presented in Table IV. The value of *D* used to calculate the diffusion currents was 1.520×10^{-5} cm.^{2} sec.$^{-1}$.[26] Taking *D* for cadmium as 1.520×10^{-5} cm.^{2} sec.$^{-1}$, $I\ (= -607nd^{1/2})$ works out to be −4.73. Thus if the equation for diffusion current held rigorously, this is the value one would obtain for the diffusion current constant. Contrary to what one would expect on the basis of theory, the results presented indicate that *I* is not entirely independent of the supporting electrolyte and of the drop time.

Table V presents the data for zinc amalgams. In this case, as has been stated, the value of *D*

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[22] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 34.

[23] D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

[24] It should be noted that in the derivation of equation (4) the same limitations are present as in the case of the Ilkovic equation.

[25] When the average current is expressed in microamp., *C* in millimoles per liter, *m* in mg. per sec. and *t* in sec., at 25° the value 607 is correctly ascribed to *k*. This value is derived from numerical constants encountered in the derivation of the equation, the value for the Faraday and the density of the amalgam. Since the amalgams employed in this study are very dilute, the density of the amalgam was equated to the density of mercury at 25°, the value 13.53 grams per cc. being used.

[26] E. Cohen and H. R. Bruins, *Z. physik. Chem.*, **109**, 397 (1924).

[27] F. Weischedel, *Z. Physik*, **85**, 29 (1933).

TABLE IV

DIFFUSION CURRENT CONSTANT DATA FOR CADMIUM AMALGAMS IN VARIOUS SUPPORTING ELECTROLYTES

Concn. amalgam, %	i_d, microamp. Obsd.	Calcd.	t, sec.	$m^{2/3}t^{1/6}$	$i_d/Cm^{2/3}t^{1/6}$
	Supporting electrolyte 0.1 *M* KCl				
0.00109	−9.03	−8.94	4.87	1.44	−4.78
.00109	−8.88	−8.90	4.94	1.43	−4.72
.00183	−15.18	−14.2	2.44	1.37	−5.05
.00207	−18.13	−18.0	4.14	1.53	−4.76
.00219	−20.24	−17.7	3.01	1.41	−5.43
.00219	−18.78	−18.4	5.14	1.47	−4.84
.00254	−22.46	−19.9	2.66	1.38	−5.34
.00287	−24.97	−22.9	2.62	1.39	−5.17
.00358	−33.23	−31.0	4.71	1.52	−5.08
.00358	−30.94	−28.4	2.78	1.39	−5.16
	Supporting electrolyte 0.1 *M* KNO_3				
0.00207	−18.61	−17.9	4.31	1.51	−4.94
.00254	−22.02	−20.2	2.92	1.40	−5.15
	Supporting electrolyte 1 *M* NH_3–1 *M* NH_4Cl				
0.00207	−18.73	−18.5	5.08	1.57	−4.79
.00219	−19.29	−19.4	5.54	1.56	−4.71
.00254	−22.10	−22.2	5.05	1.53	−4.72
.00287	−26.21	−25.5	5.07	1.56	−4.86
.00358	−31.34	−31.5	5.14	1.54	−4.72
	Supporting electrolyte 1 *M* KI				
0.00207	−17.53	−17.5	4.07	1.48	−4.75
.00254	−20.60	−20.8	3.45	1.44	−4.69
	Supporting electrolyte 0.5 *M* NaK tartrate				
0.00207	−19.12	−17.9	3.95	1.52	−5.06
.00219	−19.26	−18.4	4.95	1.48	−4.95
.00287	−26.28	−25.0	4.50	1.53	−4.97
	Supporting electrolyte 1 *M* KCN				
0.00207	−17.93	−17.9	4.42	1.51	−4.75
.00287	−25.70	−25.1	4.62	1.53	−4.84
.00287	−25.48	−25.2	4.68	1.54	−4.79

used to calculate the diffusion currents was 1.67×10^{-5} cm.^{2} sec.$^{-1}$.

TABLE V

DIFFUSION CURRENT CONSTANT DATA FOR ZINC AMALGAMS IN VARIOUS SUPPORTING ELECTROLYTES

Concn. amalgam, %	i_d, microamp. Obs.	Calcd.	t, sec.	$m^{2/3}t^{1/6}$	$i_d/Cm^{2/3}t^{1/6}$
	Supporting electrolyte 1 *M* NH_3–1 *M* NH_4Cl				
0.00048	−7.86	−7.51	4.50	1.52	−5.19
.00182	−30.00	−28.8	5.04	1.54	−5.18
	Supporting electrolyte 1 *M* NaOH				
0.00048	−7.64	−7.66	4.76	1.55	−4.95
.00182	−28.65	−28.3	5.29	1.51	−5.02
	Supporting electrolyte 1 *M* KCN				
0.00048	−7.60	−7.55	4.34	1.53	−4.99

Using the aforementioned value of *D*, *I* turns out to be −4.97. Since *D* for zinc should be greater for very dilute amalgams, it is not surprising that the average observed diffusion current constant is slightly greater than the calculated constant.

Although reliable values for the diffusion coefficients of lead, copper and thallium are not available in the literature, the results of the polarographic study on dilute amalgams of these metals are reported in Tables VI, VII and VIII since they are pertinent to the discussion.

TABLE VI

DIFFUSION CURRENT CONSTANT DATA FOR LEAD AMALGAMS IN VARIOUS SUPPORTING ELECTROLYTES

Concn. amalgam, %	i_d, microamp. obs.	t, sec.	$m^{2/3}t^{1/6}$	$i_d/Cm^{2/3}t^{1/6}$
	Supporting electrolyte 0.1 *M* KCl			
0.00158	−6.65	4.78	1.57	−4.13
.00227	−7.14	0.82	1.1	−4.5
.00227	−7.26	1.25	1.14	−4.31
.00304	−12.56	4.76	1.54	−4.11
	Supporting electrolyte 0.5 *M* NaK tartrate			
0.00158	−7.15	5.75	1.62	−4.29
.00227	−7.32	3.15	1.23	−4.00
.00304	−12.74	5.11	1.50	−4.28
.00304	−12.19	5.50	1.48	−4.15
.00304	−11.65	5.65	1.44	−4.07
	Supporting electrolyte 1 *M* NaOH			
0.00158	−6.63	5.00	1.57	−4.11
.00304	−11.16	6.19	1.44	−3.91
	Supporting electrolyte 0.1 *M* HCl			
0.00227	−6.69	0.68	1.0	−4.5

TABLE VII

DIFFUSION CURRENT CONSTANT DATA FOR COPPER AMALGAMS IN VARIOUS SUPPORTING ELECTROLYTES

Concn. amalgam, %	i_d, microamp. obs.	t, sec.	$m^{2/3}t^{1/6}$	$i_d/Cm^{2/3}t^{1/6}$
	Supporting electrolyte 0.5 *M* NaK tartrate			
0.00027	−3.43	3.98	1.48	−3.98
.00027	−3.37	4.52	1.49	−3.89
.00027	−3.37	4.78	1.49	−3.89
.00027	−3.32	4.83	1.47	−3.90
.00027	−3.22	4.52	1.44	−3.85
.00111	−11.45	1.41	1.24	−3.89
.00111	−12.23	1.95	1.31	−3.95
.00151	−19.40	3.56	1.47	−4.10
.00189	−20.49	2.20	1.27	−3.99
	Supporting electrolyte 0.1 *M* KNO_3			
0.00151	−19.12	3.55	1.48	−4.01
	Supporting electrolyte 1 *M* NH_3–1 *M* NH_4Cl			
0.00151	1st wave −9.48	5.09	1.55	−1.90

Omitting results in which *t* was less than one second, the average diffusion current constants for lead, copper and thallium are −4.14, −3.95 and −1.91, respectively, and the corresponding diffusion coefficients ($D = (I/607n)^2$) are 1.16, 1.06 and 0.99×10^{-5} cm.^{2} sec.$^{-1}$.

Since in all the amalgams studied the metals

TABLE VIII

DIFFUSION CURRENT CONSTANT DATA FOR THALLIUM AMALGAMS IN VARIOUS SUPPORTING ELECTROLYTES

Concn. amalgam, %	i_d, microamp. obs.	t, sec.	$m^{2/3}t^{1/6}$	$i_d/Cm^{2/3}t^{1/6}$
Supporting electrolyte 0.1 *M* KCl				
0.00287	−5.79	6.46	1.63	−1.87
Supporting electrolyte 0.1 *M* KNO_3				
0.00216	−4.10	4.50	1.52	−1.89
.00287	−4.98	2.10	1.34	−1.96

were present in mercury to but a few parts per million, one would expect that in multi-component or composite amalgams each metal would diffuse at the same rate as in the simple amalgams and that interatomic effects would be negligible. However, the indications are that this is not the case. The possibility of the formation of intermetallic compounds has already been mentioned. The data for composite amalgams in Table IX show quite definitely that excessive diffusion currents are flowing in the case of cadmium and lead (relative to the behavior of these metals in simple amalgams). Much additional evidence not presented here indicates that in the same medium somewhat higher values are obtained for the diffusion current constants of cadmium and lead in multi-component amalgams than for the same metals in simple amalgams.

TABLE IX

DIFFUSION CURRENT CONSTANT DATA FOR COMPOSITE AMALGAMS

Supporting electrolyte	$i_d/Cm^{2/3}t^{1/6}$ Zinc (1.186 mM/l.)	Cadmium (1.035 mM/l.)	Copper (1.375 mM/l.)
Composite amalgam No. 1			
0.1 *M* KNO_3	−4.85	−5.49	
.5 *M* NaK tartrate	−5.20	−5.27	−4.07
	Zinc (1.696 mM/l.)	Lead (1.097 mM/l.)	
Composite amalgam No. 2			
0.1 *M* KNO_3	−4.57	−4.88	
.5 *M* NaK tartrate	−4.86		
.1 *M* HCl	−5.04	−4.80	
1 *M* NaOH	−4.80	−4.99	

Consideration of Certain Factors Affecting Diffusion Current

Concentration of Amalgam.—Although it is difficult to set a definite upper limit to the concentration of amalgams studied polarographically, it is obvious that one of the determining factors is the ability of the amalgams to drop regularly through the capillary. Heyrovsky and Kalousek[2] found that amalgams having a concentration greater than 0.005% adhered to the walls of the capillary with irregular dropping and eventual stopping of the capillary resulting. However, Lingane[3] succeeded in dropping an approximately 0.01% cadmium amalgam. In the present investigation amalgams as concentrated as 0.00782% were dropped successfully.

Rate of Flow of Amalgam.—According to Loveridge[28] the rate of flow of mercury from a capillary is reasonably independent of supporting electrolyte but in air m is significantly larger than in aqueous solutions, the difference varying from 0.5 to 3.5%. As regards amalgams, the rate of flow is about as independent of medium as is pure mercury. The m values for amalgams in air were invariably higher than those in solution, as indicated by the data for cadmium amalgams in Table X.

TABLE X

RATE OF FLOW OF CADMIUM AMALGAMS IN VARIOUS MEDIA

Temp. 25°, $h = 41.5 \pm 0.2$ cm.

Concn. amalgam, %	m (mg. per sec.) Air	H_2O	0.1 *M* KCl	0.1 *M* KNO_3	1 *M* NH_3–1 *M* NH_4Cl	0.5 *M* NaK tartrate
0.00014	1.335		1.300			
.00120	1.336	1.290	1.284	1.305	1.289	1.264
.00183	1.327	1.270	1.276	1.255		
.00245	1.335	1.314	1.308	1.308	1.293	1.296
.00326			1.284		1.268	1.267
.00490	1.344	1.330	1.327	1.334	1.329	1.321

The data for the other simple amalgams and the composite amalgams are essentially in agreement with those in Table X, showing that m is reasonably independent of the nature of the amalgam. No direct comparison of these data with the data in Table X is possible because all the m values were determined under a certain applied voltage. The data presented in Table X are for the amalgam dropping into the medium in question with no potential applied.

Drop Time.—According to the Ilkovic equation the diffusion current is proportional to the one-sixth power of the drop time. However, recent studies[29,30] have shown that this relation is not strictly correct especially at small drop times when excessive diffusion currents are obtained. With dropping amalgam electrodes as a general rule high diffusion currents were obtained at short drop times. However, it is difficult to predict accurately the effect of drop time for amalgam electrodes since the diffusion currents, as discussed below, were not always independent of the nature of the supporting electrolyte. In some cases there was a systematic increase in diffusion current constant with decreasing drop time, *e. g.*, lead amalgams in 0.1 *M* potassium chloride (Table VI).

Supporting Electrolyte.—According to equation (4) in the case of amalgams the diffusion current is independent of the supporting electrolyte. However, the data which have been

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[28] B. A. Loveridge, Ph.D. Thesis, Harvard University, 1947.

[29] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1944).

[30] J. K. Taylor, R. E. Smith and I. L. Cooter, *J. Res. Natl. Bur. Stds.*, **42**, 387 (1949).

presented for simple amalgams do not appear to indicate that the diffusion current is entirely independent of the solution with which the amalgam is in contact. Thus for cadmium amalgams good agreement between observed and calculated currents was obtained in the supporting electrolytes 1 *M* ammonia–1 *M* ammonium chloride, 1 *M* potassium iodide and 1 *M* potassium cyanide. The currents observed in 0.1 *M* potassium nitrate and 0.5 *M* sodium potassium tartrate were consistently high by several per cent. in spite of the fact that the drop times were within the recommended limits. In 0.1 *M* potassium chloride the results were not consistent for amalgams having a similar drop time although the trend seemed to be toward high diffusion currents. Although the drop times for the zinc amalgams were within the narrow range 4.34–5.29 sec., the diffusion currents obtained in 1 *M* ammonia–1 *M* ammonium chloride were on the average 4.42% high whereas those in 1 *M* sodium hydroxide and 1 *M* potassium cyanide came close to the calculated values. These results indicate that the attainment of diffusion control is facilitated by an electrolyte which is especially receptive to the metal ions produced at the dropping amalgam anode. As stated above, cadmium amalgams gave the best results in ammoniacal, iodide and cyanide solutions and it is with these media of all the media studied that cadmium forms the strongest complexes. Although the case for zinc is not as convincing as that for cadmium, the results show that the observed and calculated currents agree best in those media in which a sizable shift in the half-wave potential has occurred.

When the amalgams were polarographed in solutions containing ions of the amalgamated metal, combined cathodic–anodic waves were obtained. The height of the cathodic portion was strictly proportional to the metal ion concentration as indicated in Fig. 8.

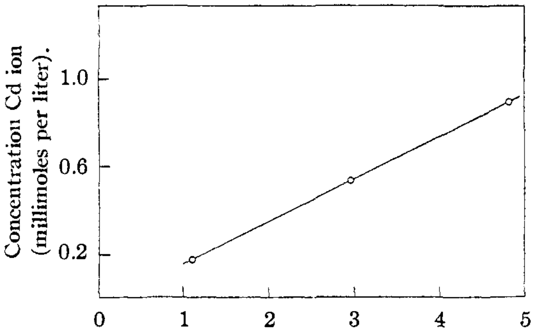

Fig. 8.—Relation between current and concentration of cadmium ion for 0.00109% cadmium amalgam dropping into 0.1 *M* potassium chloride 0.01% in gelatin and containing cadmium ions.

The relation between $i_d/m^{2/3}t^{1/6}$ and concentration of amalgam for cadmium, lead and copper amalgams is shown in Fig. 9.

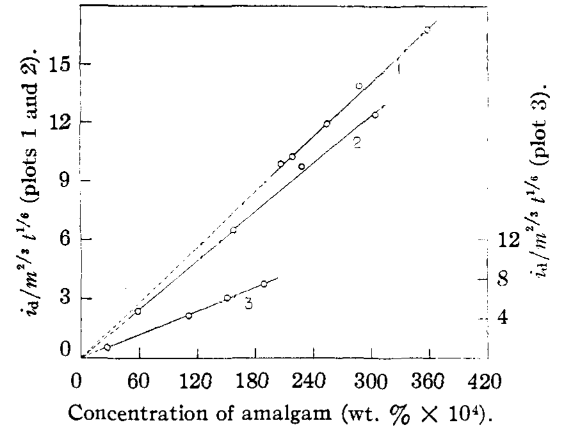

Fig. 9.—Relation between $i_d/m^{2/3}t^{1/6}$ and concentration for various amalgams: 1, cadmium amalgam in 1 *M* ammonia–1 *M* ammonium chloride; 2, lead amalgam in 0.1 *M* potassium chloride; 3, copper amalgam in 0.5 *M* sodium potassium tartrate.

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Summary

1. A quantitative study of the polarographic behavior of simple and composite amalgams of zinc, cadmium, thallium, lead and copper is presented.

2. An apparatus and technique are described whereby amalgams of known concentration can be prepared and dropped through a capillary in the virtual absence of air.

3. A comparison of the half-wave potentials for amalgam anodes with the corresponding cathodic half-wave potentials at the dropping mercury electrode in the same media gives valuable indications as to the reversibility of electrode processes.

4. Diffusion coefficients for individual metals through mercury may be derived from the polarographic data on amalgam anodes. In certain cases the results strongly suggest that there may be compounds between metals dissolved in mercury, even at great dilutions. The diffusion coefficient for thallium in mercury is estimated to be roughly half the magnitude of that for thallous ion in water. The diffusion coefficients for zinc, cadmium, lead and copper in mercury are appreciably larger than those for the corresponding hydrated ions in aqueous media.

5. The concentration of a single metal in mercury may be estimated to good approxima-

tion by anodic polarography. When several metals are present in a dilute amalgam the quantitative estimation of the individual metals by anodic polarography is less satisfactory than for a single metal.

PRINCETON, N. J. RECEIVED APRIL 18, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

$ZnSO_4 \cdot 7H_2O$. $ZnSO_4 \cdot 6H_2O$. Heat Capacities, Entropies and Crystal Perfection at Low Temperatures. Heats of Solution and Transition

BY R. E. BARIEAU AND W. F. GIAUQUE

The work reported in this paper is related to a study of magnetic properties of compounds of the elements of the first transition period, particularly the heptahydrates of ferrous, cobaltous and nickel sulfates. The splitting of the energy levels of these paramagnetic ions is attributed to the electric fields of the water molecules which surround the ion. It is customary to assume that the water molecules are arranged in a definite crystalline pattern about the ion so that the arrangement can be considered to have some simple form of symmetry with respect to the electric fields due to the water molecules. While this is undoubtedly true in most cases there may be numerous exceptions. There are few data relating to this point.

It has been shown experimentally by Giauque and Stout[1] that the hydrogen bond structure of ice is completely random with respect to the four tetrahedral bond positions around each oxygen, as suggested by Bernal and Fowler,[2] and by Pauling,[3] who predicted the entropy discrepancy corresponding to the assumed disorder.

Long and Kemp[4] have shown that the deuterium bond disorder in deuterium oxide ice is the same as that which occurs in ordinary ice.

Pitzer and Coulter[5] have found a discrepancy in the entropy of $Na_2SO_4 \cdot 10H_2O$ which is probably due to disordered hydrogen bonds. In any case, the entropy discrepancy proves that the crystal is disordered in some respect.

The electric fields of a central ion about which the water molecules are arranged are certainly a powerful influence in producing perfect order but this alone may well be insufficient to prevent one or more of the water molecules from forming hydrogen bonds in more than one way.

$ZnSO_4 \cdot 7H_2O$ was selected for investigation because this substance, being diamagnetic, would avoid the additional complications which can arise in paramagnetic systems. Otherwise, this substance is rather similar to the other divalent heptahydrated sulfates of the first transition series.

Quite aside from the desirability of knowing that a crystal is perfect before attempting to explain various specific characteristics, such as magnetic properties, the problem is outstanding in the application of the third law of thermodynamics. Since the work on ice a considerable amount of work has been started in this Laboratory on related problems. Forsythe and Giauque[6] have presented substantial evidence which indicates that nitric acid and its mono- and trihydrates attain zero entropy and thus crystal perfection at the absolute zero. Other work was interrupted by the war and has only recently been resumed.

The present work, which includes the heat capacities of $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$, to low temperatures, and their heats of solution, was intended as an investigation of both the hepta- and hexahydrates of zinc sulfate; however this latter substance underwent a thermodynamically irreversible transformation at low temperatures. This arrangement in the solid was so slow that it is questionable whether the data obtained on the hexahydrate can be used as evidence in the original objective.

We may say at once that $ZnSO_4 \cdot 7H_2O$ has been found to obtain an ordered arrangement at low temperatures and that the measurements on the hexahydrate, such as they are, give some indication that this substance may retain disorder.

Preparation of $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$.—The sample of zinc sulfate heptahydrate was prepared by bubbling purified dry air through a saturated solution of Baker C. P. zinc sulfate heptahydrate at room temperature.

After a considerable amount of solid had precipitated, the solution, in a 2-liter flask, was cooled to about 0° in the presence of the solid, and then the crystals of $ZnSO_4 \cdot 7H_2O$ were filtered off. The above method was followed because Bury[7] has shown that it is possible to prepare a metastable monoclinic form of $ZnSO_4 \cdot 7H_2O$ below 25°. Bury[7] found that the metastable monoclinic form and the hexahydrate are in equilibrium with the saturated solution at 24.8°, and that the stable rhombic $ZnSO_4 \cdot 7H_2O$ and the hexahydrate are in equilibrium with the saturated solution between 38 and 39°.

Proof that the above method of preparation gave the stable rhombic form in the present work is furnished by the fact that during the heat capacity measurements no isothermal absorption of heat was observed at 25°, while there was such an absorption of heat between 38 and 39°. The temperature of the transition was determined as

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[1] Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936).

[2] Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[3] Pauling, THIS JOURNAL, **57**, 2680 (1935).

[4] Long and Kemp, *ibid.*, **58**, 1829 (1936).

[5] Pitzer and Coulter, *ibid.*, **60**, 1310 (1938).

[6] Forsythe and Giauque, *ibid.*, **64**, 48, 3069 (1942); **65**, 2379 (1943).

[7] Bury, *J. Chem. Soc.*, **125**, 2538 (1924).