[CONTRIBUTION FROM THE BAKER LABORATORY, CORNELL UNIVERSITY]

The Electrolytic Decomposition of Dilute Amalgams

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A study has been made of the anodic decomposition of dilute amalgams and of the general behavior of amalgam electrodes when the decomposition is achieved by: (a) discharge through a resistance at constant applied potential, (b) under the influence of an intermittent constant current, or (c) under conditions of constant anode potential. It was found that amalgams of cadmium and thallium can be completely decomposed and that a general insight into the phenomena of decomposition under conditions of constant anode potential, or through a resistance, can be found in the application of the Nernst equation, Ohm's law and Faraday's law with the conventional concentration polarization corrections. It was found, however, that cadmium is not reversible in this type of experiment, in that there is a non-polarization contribution to the overpotential. It was also found that the efficiency of the constant current decomposition was much greater than could be explained in view of the calculated effect of polarization. It is proposed that this efficiency is due to the formation of an adherent film which acts as an intermediate for the storage and transfer of electrons. Studies of bismuth, cobalt and nickel indicate that the deposited metals cannot be anodically oxidized without decomposing mercury.

As is generally true, the development of understanding in electrochemistry is dependent upon the utility of that understanding. This, coupled with the analytical developments of the mercury electrode in the fields of polarography and mercury cathode separations, has resulted in the accumulation of a great deal of information and of a generally adequate understanding of the problems involved in the deposition of metals into a mercury cathode. Far less consideration, however, has been given to the complementary problem of the anodic dissolution, of stripping, of metals from amalgams.

L. B. Rogers[1] has derived a set of equations for the calculation of the equilibrium distribution of a metal between the aqueous and mercury phases as a function of the cathode potential, the polarographic half-wave potential, and the volume ratio of the phases. Rogers and Merritt[2] have tested these equations for thallium and cadmium. Coriou, Hure and Meunier[3] made a study of the anodic decomposition of various amalgams in a sulfuric acid medium with particular attention to the completeness of decomposition and the behavior of the anode potential as a function of current density at currents which were low compared with the limiting diffusion current. Kozlovsky,[4] Tsyb,[5] and Ruzina,[6] have made studies of the anodic and cathodic behavior of several ion–amalgam systems but only for cases involving high concentrations and high currents. Schmidt has recently studied the isolation of heavy metals from vanadyl salts by an anodic stripping procedure.[7]

As a preliminary to a study of the analytical application of amalgam decompositions, the present work deals with the completeness of amalgam decompositions and with the general behavior of amalgam electrodes when decomposition is achieved by: (a) discharge through a resistance at fixed applied potentials, (b) under the influence of an intermittent constant current, or (c) under conditions of constant anode potential.

Experimental

The cell used in this work was designed to handle a mercury volume of 10 ml., with an area of 14 square centimeters, and an aqueous volume of 100 ml. Provision was made for deaeration by introducing nitrogen through the hollow stirring shaft, which was driven at 540 r.p.m. A calomel probe was placed near the pool for potential measurement, while a second working electrode consisted of a silver wire in molar potassium chloride. This silver electrode was isolated from the pool by a large sintered disk and an agar bridge.

The various electrical requirements were met in the following ways. Constant applied potentials were obtained from a 6-volt storage battery through a 70-ohm voltage divider. This same voltage divider was used in experiments requiring a constant anode potential, but in this case the output of the divider was manually adjusted as required to keep the anode potential fixed. Constant currents were obtained from a 90 to 180 volt battery supply through a swamping resistance.

Electrode potential measurements were obtained with a Leeds and Northrup student potentiometer. Current values were calculated from the *IR* drop across a 150-ohm precision resistance, as measured with a Rubicon potentiometer.

Recorded data were obtained with a Leeds and Northrup Speedomax recorder. Current measurements were obtained by placing the recorder across an accurate resistance. In making potential measurements, the recorder was attached to a high-resistance voltage divider and the scale adjusted, by means of the sensitivity regulator, to give agreement with the potentiometer.

For polarographic type measurements, the polarizer described by Streuli and Cooke[8] was used in conjunction with the recorder. In order to avoid errors due to ohmic potential drop, the time axis of the chart was not assigned a fixed potential scale. Instead the potential was followed with the potentiometer and signal marks were obtained at convenient intervals by increasing or decreasing the current measuring resistance momentarily.

The amalgams were prepared by applying a constant potential, usually of the order of one volt, across the pool and the silver–silver chloride electrode. The plating was better than 99% complete after one to two hours, though longer periods were used in preparing amalgams for coulometric titrations.

In order to determine the completeness of plating, the electrolytic current may be observed as a function of time, since it decreases logarithmically as plating proceeds. However, the residual current is of the order of 5 to 10 μ amp. and contains a great deal of hash. For this reason it was found more expedient to follow the potential of the pool, which approaches a constant value as the plating becomes complete. This may be done either by removing the plating potential and reading the rest value of the electrode or, if the source of the applied potential is stable enough, simply by reading the potential of the pool.

Except where otherwise indicated, a supporting electrolyte of tenth molar potassium chloride was used throughout this work.

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[1] L. B. Rogers, *J. Electrochem. Soc.*, **99**, 267 (1952).

[2] L. B. Rogers and C. Merritt, Jr., *ibid.*, **100**, 131 (1953).

[3] H. Coriou, J. Hure and N. Meunier, *Anal. Chim. Acta*, **9**, 171 (1953).

[4] M. T. Kozlovsky and P. P. Tsyb, *J. Appl. Chem.*, *USSR*, **23**, 1285 (1950) (English translation).

[5] P. P. Tsyb and M. T. Kozlovsky, *ibid.*, **24**, 840 (1951).

[6] M. T. Kozlovsky, P. P. Tsyb and E. I. Ruzina, *ibid.*, **24**, 882 (1951).

[7] W. E. Schmidt, Univ. Microfilms, No. 8089, thru *Chem Abs.*, **48**, 9863 (1954).

[8] C. A. Streuli and W. D. Cooke, *Anal. Chem.*, **25**, 1691 (1953).

Completeness of Stripping.—While the equations of Rogers[1] indicate that an amalgam may be decomposed with virtual completion by the application of a potential a few tenths of a volt more positive than the polarographic half-wave potential, a method was sought which might directly test the validity of the equation in this respect. Comparison of polarographic analysis of a cadmium solution before plating, after plating and after stripping, indicate that both the plating and the stripping processes were complete. However, the precision of polarographic results was not adequate to allow any conclusion beyond saying that the stripping process was at least 95% complete.

Decomposition through a Resistance at Fixed Applied Potential.—In these experiments a fully-plated amalgam was connected through a resistance to the silver–silver chloride electrode and the current was recorded as a function of time. Where it was desired to vary the applied potential, the output of a low resistance voltage divider was inserted in the appropriate manner.

Assuming that the only overpotential effect at the pool is concentration polarization, it is possible to derive expressions for the potential and current as a function of time.

In the following development, the prime refers to the amalgam phase and the double prime refers to the aqueous phase.

C'_s = concn. of amalgam at the interface
C''_s = concn. of aq. phase at the interface
C' = bulk concn. of the amalgam
C'' = bulk concn. of the aq. phase
I = current density
A = area of the pool
M = total no. of moles present
v' = vol. of the amalgam
v'' = vol. of the aq. phase

The current is taken as positive for cathodic processes at the pool and all concentrations are in moles per cubic centimeter.

The Nernst equation is used in the following approximate form

$$E = E_{1/2} + \frac{RT}{nF} \ln C''_s/C'_s \qquad (1)$$

where $E_{1/2}$ is the potential of the pool, measured with respect to the second working electrode, when the interface concentrations in the two phases are the same. This is equivalent to the half-wave potential used in polarography.

Using the conventional expressions[9] for the concentration polarization, one obtains the equations

$$C'_s = C' + K/k' \qquad (2)$$

$$C''_s = C'' - I/k'' \qquad (3)$$

where k' and k'' are constants determined by the diffusion constant and the thickness of the diffusion layer.

Inserting (2) and (3) into (1)

$$E = E_{1/2} + RT/nF \ln (C'' - I/k'')/(C' + I/k') \qquad (4)$$

If at time $t = 0$ all the metal is assumed to be in the amalgam, then at any later time

$$C'' = -A/v''nF \int_0^t I \, dt \qquad (5)$$

$$C' = M/v + A/v'nF \int_0^t I \, dt \qquad (6)$$

When (5) and (6) are inserted into (4) the following expression is obtained for the potential of the pool at any time

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{-A/v''nF \int_0^t I \, dt - I/k''}{M/v' + A/v'nF \int_0^t I \, dt + I/k'} \qquad (7)$$

On the assumption that only concentration polarization is affecting the current flow, the resistance may be assumed to be linear and the current is given by

$$I = E/r \qquad (8)$$

These equations are invalid when the potential becomes positive enough for mercury dissolution to contribute to the current. However, when they are applied it is found that the value of I/k' in the denominator is such that the equation reduces to the case of diffusion limitation before the potential becomes positive enough to allow mercury dissolution. Consequently, that portion of the curve in which this difficulty would arise is calculated as a diffusion limited, logarithmic decay curve.

In order to apply these equations, it is necessary to obtain values for k' and k''. When this was done on the basis of the limiting current values obtained when the pool was subjected to a varying potential, as in polarography, the following values were obtained: k', 2600 amp. cm./mole, and k'', 1020 amp. cm./mole. The value of k' may also be found from the slope of the logarithmic decay curve obtained in constant potential decompositions. The value obtained from this slope (Fig. 6) was 2000 amp. cm./mole. This value was accepted for the calculation since it would be expected to be more accurate, being independent of any knowledge of the concentration and being determined by all the points on the curve rather than a single measurement.

It was also found that the anodic value of the half-wave potential measured on decomposition was −0.44 *vs.* S.C.E., which differs from the cathodic value of −0.60 and the literature value[10] of −0.599.

The results of these experiments, which might be thought of as polarograms, are shown in Fig. 1. The difference in the position of the inflection points is plainly evident. The reason that the anodic wave is so drawn out is that, at the scanning speed used, a large portion of the metal in the amalgam was removed before the potential had become sufficiently positive to develop the wave. This same depletion effect explains the fall in anodic current between −0.2 and 0.0 *vs.* S.C.E.

This irreversibility is again evident in the slope of the log current *vs.* time curves for the constant potential stripping of cadmium. Since the potential of the amalgam, when measured on open circuit at the mid-point of a constant current decomposition, is in agreement with the value predicted by the usual polarographic half-wave potential, this appears to be an overpotential effect.

In the application of these equations, the observed anodic value of the half-wave potential was used. Since the second working electrode was a

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(9) S. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand, Inc., New York, p. 445 *et seq.*

(10) I. M. Kolthoff and J. J. Lingane, "Polarography," 1st. Ed., Interscience Publishers, Inc., New York, N. Y., 1941, pp. 482.

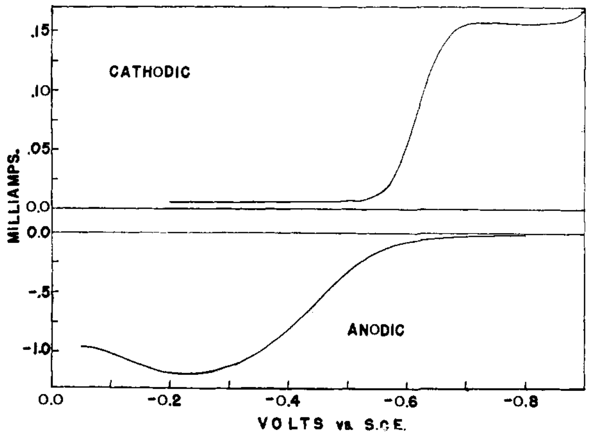

Fig. 1.—Current as a function of potential for cadmium ion at a stirred mercury cathode (cathodic) and for stirred cadmium amalgam (anodic).

silver–silver chloride electrode in molar potassium chloride, the observed value of −0.44 *vs.* S.C.E. must be corrected to −0.43 before the calculations are carried out. In view of the current dependence of the apparent half-wave potential, these calculations must be looked upon as semi-quantitative since the assumption of pure concentration polarization is no longer valid and the correct expressions should contain $E_{1/2} = f(I,t)$ rather than $E_{1/2}$ = const.

With these limitations the curve was calculated for the case of an amalgam containing 1.36×10^{-5} moles of cadmium in a volume of ten cubic centimeters being discharged through a resistance of 550 ohms into an aqueous phase of one hundred cubic centimeters.

The procedure of calculation was to begin at the point of 50% stripping and calculate the current on the assumption that polarization was negligible. Using this value to evaluate the polarization terms, a second value was determined. A third approximation produced no change from the second approximation. Subsequent points were calculated on both sides of the point of 5% stripping. In each case, the current found for the adjacent known point was used to evaluate the polarization terms. No change was observed when second approximations were tried.

At 98% stripped, polarization was better than 95%, that is the surface concentration of the metal in the amalgam was less than 5% of the bulk concentration in the amalgam. For this reason it was assumed that the remainder of the curve was the usual logarithmic decay curve of a diffusion controlled process. For this portion of the curve, the half-time for the decomposition was obtained from the log current *vs.* time curve obtained in constant potential stripping (Fig. 6).

Having obtained values of the current at various fractions stripped, the time scale was set by determining the time required for the average current between two points, for example between 10 and 15% stripped, to decompose an amount of cadmium equivalent to the difference between the two points, or in the example selected, the time required to decompose 5% of the total amount of cadmium. As indicated above, the curve beyond 98% stripped was obtained by using the value of the half-time found in constant potential stripping. This value was 48 seconds, therefore the current is halved at 48-second intervals beyond 98%.

The calculated curve is shown in Fig. 2 along with the curve observed for the decomposition of a ten cubic centimeter amalgam containing 1.36×10^{-5} mole of cadmium into 100 ml. of 0.1 *M* potassium chloride. The external resistance in this case was 500 ohms but the internal resistance of the cell was estimated to be 50 ohms on the basis of conductance measurements. Also shown on this figure, are the observed results in the case in which the external resistance was 200 ohms and the cell resistance 50 ohms. The difference caused by changing the total resistance from 550 ohms to 250 ohms is considered later in terms of equation 7.

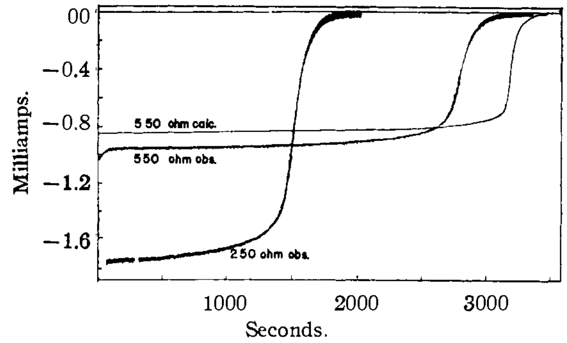

Fig. 2.—Calculated and observed current *vs.* time curves for the discharge of a cadmium amalgam through a resistance.

While the curves agree well in general form, there is a significant difference in the time of current fall and in the current during the major portion of the decomposition. While a portion of this difference might be due to an incorrect value given the cell resistance, the major difference must be attributed to the fact that the currents encountered are not large enough to cause the apparent half-wave potential to be −0.44 *vs.* S.C.E. While the lack of a correct expression for $E_{1/2}$ led to this error, it is apparent that it would have little effect on the shape of the curve since there is little variation in the current until the point of diffusion limitation is reached.

While it is felt that the equations developed are basically correct in their description of the process, the lack of a functional relationship between the apparent half-wave potential and the concentration and current, combined with the awkward nature of the calculations, limit the use of these equations to a qualitative understanding of the effect of the various conditions on the current–time curve.

If the resistance in the external circuit is increased there is the direct effect of reducing the current. This reduction in current in turn reduces the importance of the polarization terms with the result that the drop in current does not occur until the decomposition is more nearly complete. This effect is shown for the 250 and 550 ohm cases in Fig. 2.

Reducing the concentration of the amalgam does not effect the initial current since the ratio, and not the total concentration, determines the potential. However, the drop in current does occur earlier since the polarization terms are larger compared with the concentration terms. If there is a sufficient reduction in the concentration together with a low circuit resistance, the relatively constant initial current portion of the curve disappears.

Variation of the applied potential amounts to an arbitrary variation of the half-wave potential which should be used in equations 1, 4 and 7. The direct result is an increase or decrease in the initial current with accompanying effects on the magnitude of the polarization terms.

If a thallium amalgam is decomposed through an external resistance of 50 ohms, the result, compared with the decomposition of a cadmium amalgam through the same resistance, is a lower initial current. The half-waves are nearly equal, if allowance is made for the apparent irreversibility of the cadmium system. However, since the currents are high, the fact that the thallium reduction is a one electron change while the cadmium reduction is a two electron change, leads to a greater polarization effect in the case of thallium. Also, since the molar concentrations are of the same order of magnitude, the thallium curve drops off sooner.

Decomposition of Amalgams under the Influence of a Constant Current.—The procedure in this series of experiments was to decompose a fully plated amalgam with an intermittent constant current. Measurements of the potential of the pool were made during rest periods between the current increments. If these potentials are plotted as a function of the cumulative time that the current is applied, the result is similar to the curve obtained in a classical potentiometric titration, as is shown in Fig. 3. The potential changes slowly during the larger portion of the process, the value being close to that predicted by the polarographic half-wave potential and the volume ratio when the amalgam is half decomposed. Near the end-point the potential rises rapidly to that of the mercurous chloride, tenth molar potassium chloride electrode.

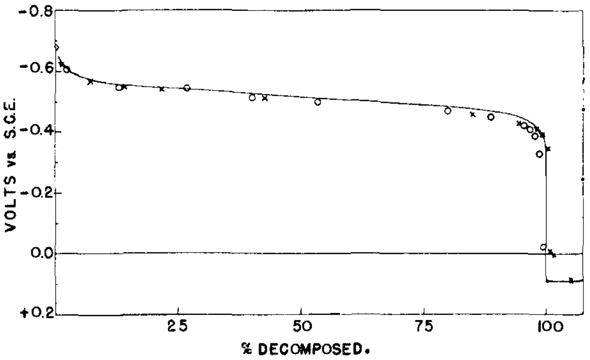

Fig. 3.—Calculated titration curve for thallium amalgam. The circles are observed points for the titration of a 5 × 10^{-4} M amalgam with a current of 1.14 ma. and the x's are observed points for the titration of a 5 × 10^{-4} M amalgam with a current of 2.20 ma,

Considering this to be a constant current coulometric titration with a potentiometric end-point, a series of titrations were made on varying amounts of cadmium and thallium. The results of these titrations are presented in Tables I and II.

TABLE I

COULOMETRIC TITRATIONS OF CADMIUM AMALGAMS

Current. ma.	Time. sec.	Mg Found	Mg Taken	Error. mg.
4.57	289	0.770	0.770	0.0
4.52	148	.338	.385	+ .003
2.30	298	.399	.385	+ .014
2.30	109	.147	.154	− .007
2.30	55.2	.074	.077	− .003

TABLE II

COULOMETRIC TITRATIONS OF THALLIUM AMALGAMS

Current. ma.	Time, sec.	Mg, mg. Found	Mg, mg. Taken	Error. mg.
2.19	223	1.03	1.02	+0.01
1.14	426	1.02	1.02	.0
1.14	95	0.226	0.203	+ .023
0.570	175	0.210	0.203	+ .007

In agreement with the view of the constant current decomposition of amalgams as coulometric titrations, it is possible to calculate a theoretical titration curve which agrees well with the observed results.

For the purposes of calculation, the reaction was considered as the titration of the amalgam with mercurous ion since, as explained below, an intermediate appears to be formed which is probably mercurous chloride. The two potentials then used were the standard potential of the mercury–mercurous ion couple and the half-wave potential of the metal in the amalgam.

When the case of thallium was attempted in this manner it was found that the theoretical end-point was at a value more positive than allowed by the presence of 0.1 M potassium chloride. This means that the end-point will be theoretically obscured by the limiting potential of the mercury–mercurous chloride electrode. However, this interference is not predicted until the titration is complete to the extent of over 99.999%. As a result the only practical effect is that the curve is not expected to be symmetrical.

In Fig. 3 this theoretical curve is presented along with the results of two titrations of thallium. While the general agreement is good the observed values do exhibit a curvature in the region where the potential approaches the limiting potential of the mercurous chloride electrode.

Considering the high current densities compared with the concentrations of the amalgams, there must be an intermediate formed, particularly near the end-point of the titrations. This intermediate appears to be a solid film, probably mercurous chloride, which is laid down on the surface of the pool during the periods of stripping.

From the open circuit potentials the process appears as a normal potentiometric titration. However, the potential of the amalgam during stripping and following the interruption of the current has a distinctive behavior. In more dilute amalgams and at higher current densities, the pool seems to be completely polarized by the stripping current. For example, near the end-point in one titration of cadmium, the potential of the pool under the influence of a current of 4.17 ma. was 0.23 volt *versus* the S.C.E. When the current was interrupted, the potential immediately fell to 0.06 volt, then remained nearly constant for about 20 seconds before falling at an increasing rate to the steady rest potential of −0.56 volt. This series of events is shown in Fig. 4 which shows the potential of the pool as a function of time during this sequence.

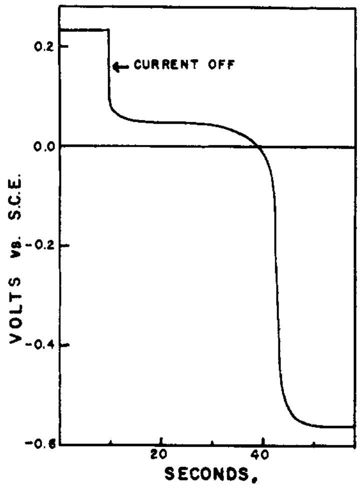

Fig. 4.—The potential of an amalgam as a function of time following the interruption of a constant current.

Coinciding with this delay in the recovery of the rest potential, which lasted as long as a minute or more in extreme cases, the visible film which formed during the stripping interval was observed to disappear.

In order to test the hypothesis that the film intermediate was a mercury compound, an amalgam of copper was decomposed into a supporting electrolyte of 0.03 *M* Versene buffered to a *p*H of 6.4. Under these conditions, the limiting process, upon polarization of the pool, would be the formation of the Versenate complex of mercury rather than the formation of mercurous chloride. When copper was stripped under these conditions, using an intermittent constant current, the delayed recovery was not observed and the potential gradually changed from that of the copper ion–copper amalgam system to that of the mercury–mercury Versenate complex.

A similar sort of evidence was obtained from attempts to titrate mixed amalgams. Instead of obtaining two sharp potential breaks, the first corresponding to the completion of decomposition of the metal with the more negative half-wave potential and the second to the completion of decomposition of the metal with the more positive half-wave potential, only the second inflection was found. The first was replaced by a gradual transition from the potential of the more negative ion amalgam couple to that of the more positive ion amalgam couple. Apparently, as the electrode becomes polarized with respect to the more negative metal, the more positive metal begins to be anodically oxidized. Since any electricity lost by this process is dispersed throughout the aqueous phase, it could only be regained by allowing the amalgam to stand on open circuit for hours.

Constant Potential Stripping.—In this series of experiments a fully plated amalgam was decomposed with the potential of the pool held constant by manual variation of the applied potential. Typical curves for cadmium and thallium are shown in Fig. 5.

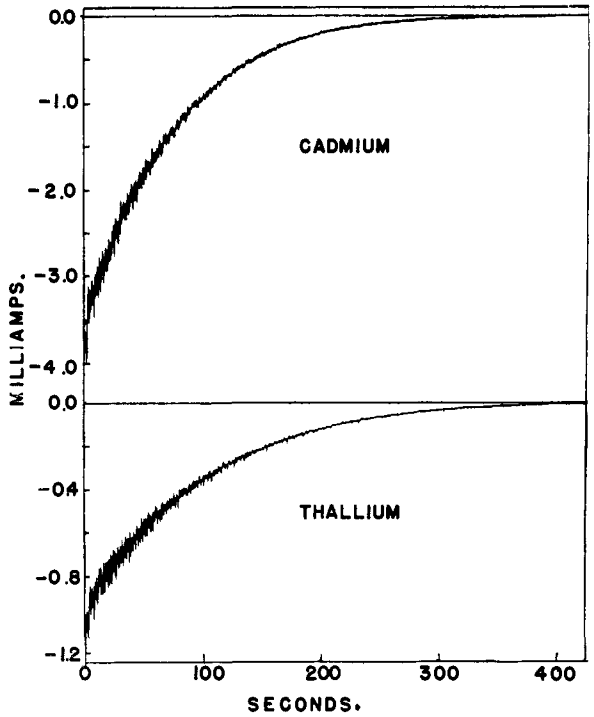

Fig. 5.—Current time curves for the decomposition of a 10^{-4} *M* cadmium amalgam at −0.1 volt *vs.* S.C.E. and a 10^{-4} *M* thallium amalgam at −0.2 volt *vs.* S.C.E.

Since it would be expected that the current would decay in the logarithmic fashion of a diffusion controlled system if the potential was sufficiently positive, the data are better represented in Fig. 6 in which the current is plotted on a logarithmic scale as a function of time.

It will be noted that the slope of the line for cadmium varies considerably when the electrode was maintained at −0.4 volt *vs.* S.C.E. This is in agreement with the observed current dependence of the half-wave potential of cadmium, since the slope is not expected to vary appreciably at potentials more than a tenth of a volt more positive than the half-wave potential. Thus, if the half-wave potential was not different from that observed in dropping mercury studies, the slope of the curve at −0.4 volt would not differ from that observed at more positive potentials.

The curvature in the case of cadmium at −0.4 volt is attributed to ohmic drop between the tip of the calomel probe and the pool. Since this run was made close to the half-wave potential, any small error in the potential of the pool would lead to a large variation in current.

The slope of the line given by the plot of the current on a logarithmic scale as a function of time

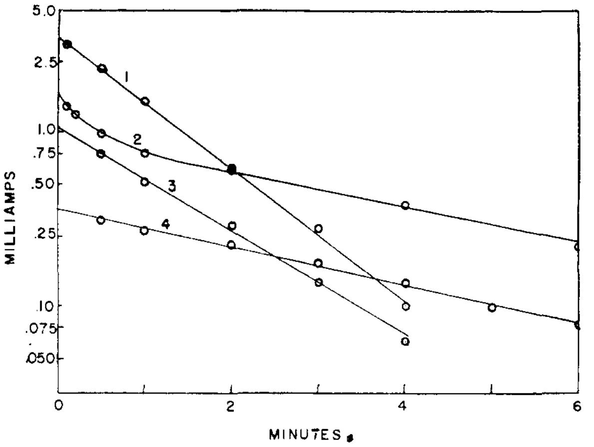

Fig. 6.—Current (log scale) as a function of time in constant potential stripping of amalgams: 1, 10^{-4} M cadmium amalgam decomposed at 0.0 volt *vs.* S.C.E.; 2, 10^{-4} M cadmium amalgam decomposed at −0.4 volt *vs.* S.C.E.; 3, 10^{-4} M thallium amalgam decomposed at 0.0 volt *vs.* S.C.E.; 4, 10^{-4} M thallium amalgam decomposed at −0.45 volt *vs.* S.C.E.

should be given by the expression $2.303\ \Delta \log I = Ak'/nFv'\ (\Delta t)$, where the symbols have the same meaning previously ascribed to them. This expression was used to calculate the value of k' which was used to calculate the theoretical curve in Fig. 3.

When attempts were made to decompose deposits of cobalt and nickel electrolytically, the results indicated that the metals could not be removed from the mercury at an appreciable rate at potentials negative enough to prevent the dissolution of mercury. This is in agreement with the findings of Coriou, Hure and Meunier.[3]

When a polarogram of nickel ion in 0.1 M potassium chloride was run at this electrode without stirring and a portion of the nickel was allowed to accumulate in the amalgam before rescanning the potential in the reverse direction, it was found that the current due to the dissolution of the nickel, if any, was obscured by the dissolution of mercury from the pool. However, when the medium was changed to 0.1 M potassium thiocyanate, an anodic polarogram showed some solution of nickel before the dissolution of mercury commenced. Attempts for normal decomposition were not successful. Preliminary experiments indicate that bismuth amalgam is similarly irreversible in a medium of 0.1 M sodium tartrate, 0.05 M sodium acetate and 0.05 M acetic acid.

Conclusion

The results of this work indicate that the electrolytic decomposition of dilute amalgams can be carried to completion in the case of polarographic reversible systems and that insight into the general phenomena may be obtained using conventional Ohm's law and Nernst equation calculations together with appropriate concentration polarization terms. In the case of the decomposition with a constant current, there is the necessity of postulating an intermediate, with indications that this intermediate is a film of mercurous chloride.

Any quantitative evaluation of results is, however, rendered hazardous by the fact that in a well agitated system there seems to be a significant departure from the ideal reversibility observed in polarographic studies.

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Ithaca, N. Y.

[Contribution from the Department of Pharmacology, University of North Carolina]

The Second Ionization of 5,5-Disubstituted Derivatives of Barbituric Acid[1]

By Thomas C. Butler, John M. Ruth and Gabriel F. Tucker, Jr.

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The apparent ionization exponents concerned with the second dissociation have been determined spectrophotometrically for a series of ten 5,5-disubstituted derivatives of barbituric acid at 38° and ionic strength of 0.1. The values of pK'_2 lie in the range of 11.77 to 12.67.

The 5,5-disubstituted derivatives of barbituric acid, a class comprising a number of compounds extensively used as hypnotic drugs, were recognized even in the earliest studies to behave as weak acids capable of forming salts. The constants for the first ionization have been measured by several investigators for numerous compounds of this type, the most comprehensive study of the problem being that of Krahl.[2] The question of a second ionization has received but little attention notwithstanding the obvious structural possibility of dissociation of protons from both of the nitrogen atoms and the evidence that has been available for some time indicating that such dissociation actually occurs. In one of the earliest synthetic investigations of this type of compound the di-silver salt of 5,5-dimethylbarbituric acid was prepared.[3] In recent years several studies of the ultraviolet absorption of 5,5-disubstituted barbituric acids in aqueous solu-

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(2) M. E. Krahl, *J. Phys. Chem.*, **44**, 449 (1940).

(3) M. Conrad and M. Guthzeit, *Ber.*, **15**, 2844 (1882).