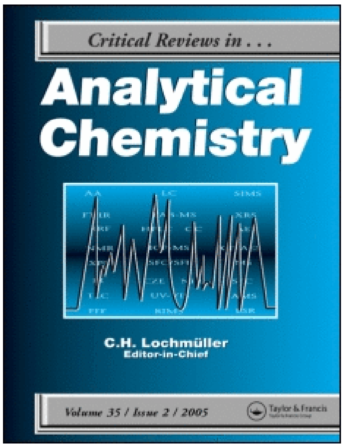

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ELECTROCHEMICAL BEHAVIORS OF METAL AMALGAMS

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INTRODUCTION

Although mercury was one of the first metals discovered by man, it has continued to attract the attention of many workers even up to the present time. This is probably due to the unique ability of mercury, which is a liquid at normal temperature, to dissolve a number of metals.

As a result of such dissolutions one gets systems that are called amalgams. The solubilities of metals in mercury are very widely different. There are some metals that are extremely soluble in mercury, such as thallium and indium, but at the same time there are some transition metals that have solubilities too low to be determined precisely using modern analytical techniques.

The name "amalgam" is also used to denote a two-phase system in which a relatively large quantity of the metal is present, as the result, for example, of the electroreduction of its ions at a mercury electrode, and remains there as a dispersed precipitate.

Some metals react with mercury to form intermetallic compounds, which very often exist in a crystalline form as a separate phase in the mercury.

For a good many years there have been investigations of even more complicated systems which, in addition to mercury, contain two or more different metals. Sometimes these metals may also form intermetallic compounds.

The interest of workers in amalgams results from several reasons. Some of these are that amalgams are applicable in metallurgy and also in various other practical fields, and that mercury and amalgams are widely applicable in various electrochemical and analytical investigations. Other methods have been used to study the properties of amalgams, but electrochemical techniques play a leading role in such studies. In part this is a result of the ease with which various amalgams can be prepared by the electroreduction of ions with mercury electrodes under proper experimental conditions. Amalgams that have been prepared electrochemically may be further investigated by electrochemical methods in order to determine the solubilities of metals and the diffusion coefficients of metal atoms in mercury, and to study the interaction of metals and mercury resulting in the formation of intermetallic compounds.

Electroanalytical methods are especially well-suited to the investigation of complex amalgams containing two or more metals in addition to mercury. The intermetallic compounds formed as a result of the chemical reaction of such metals have been especially intensively studied in recent years using these methods.

The results obtained in these studies will be briefly reviewed in the present article.

1. ELECTROCHEMICAL INVESTIGATIONS OF SIMPLE AMALGAMS

This section describes the most important of the results that have been obtained by electrochemical investigations of some simple amalgams. It is selective rather than comprehensive, partly because there are still many metals whose amalgams have not yet been investigated by these techniques.

1.1. Electrochemical Determinations of the Solubilities of Metals in Mercury

Several electrochemical techniques have applied or may be applicable, to determinations of the solubilities of various metals in mercury. Metals that are only very poorly soluble in mercury cannot be studied by these methods, but this limitation is of course shared by most non-electrochemical methods as well.

The determination of solubility is usually performed by preparing a series of amalgams containing various proportions of the metal being investigated, extending to well above the proportion that is necessary to reach the concentration of a saturated amalgam. The amalgams are successively used as electrodes in an electrolytic cell, for which some suitably chosen electrical property is measured.

If one determines the potentials of such amalgam electrodes against some reference electrode, these potentials will vary with the amalgam concentration as long as this does not exceed the saturation value (see Section 2). For saturated heterogeneous amalgams the potential should be practically constant.

The first potentiometric determinations of the solubilities of metals in mercury were performed by Tammann and co-workers,[1,2] and the technique has since been applied by others as well. As an example, Figure 1 shows the results obtained by Jangg and Kirchmayr[3] in studying the potentials of lead-amalgam electrodes in solutions containing different concentrations of lead (II).

The potential of a lead-amalgam electrode obeys the Nernst equation,

$$E = E^{0}_{Pb^{2+}/Pb(Hg)} + \frac{RT}{2F} \ln \frac{C_{Pb^{2+}}}{C_{Pb(Hg)}} \qquad (1.1)$$

up to a concentration of the metal in the amalgam which is equal to 0.9 M. If the apparent concentration of the amalgam exceeds this value, the potential remains constant since the concentration of the metal that is actually dissolved in the mercury phase does not change.

Not all of the results obtained by early authors have been confirmed by subsequent studies. It is especially difficult to obtain reliable results by this method when investigating the solubilities of metals that are poorly soluble in mercury metals (below 10^{-5} M). As is always true in potentiometric work, the investigated metal should form a redox couple with a large exchange and the exchange current is unlikely to be large if the concentration of dissolved metal is very low. In addition, care must be taken to ensure that the system reaches equilibrium before the potential is measured. There is especial danger of supersaturation in amalgams that have been prepared by

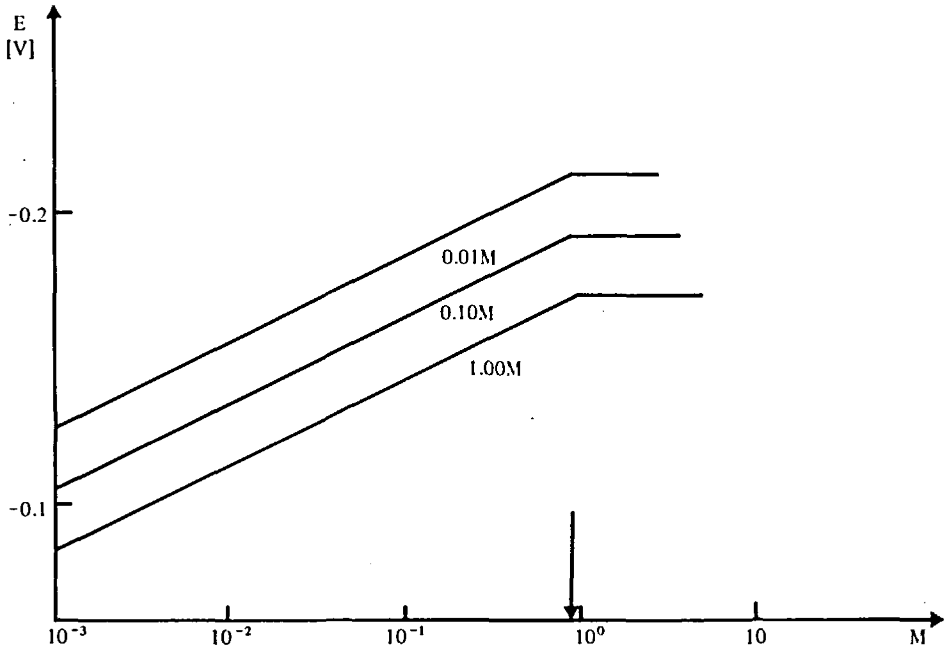

FIGURE 1. Dependences of the potentials of lead-amalgam electrodes on the concentrations of metallic lead in the amalgams.[3] The different curves were obtained with different concentrations of lead(II) ions in the solutions, and the number beside each curve gives the concentration of lead(II). The arrow indicates the concentration of the saturated amalgam.

reducing metal ions electrolytically at mercury electrodes.

When these conditions are fulfilled, the method gives results that are in fairly good agreement with those obtained in other ways, particularly for metals that are fairly soluble in mercury. This is shown by Table 1, where the results obtained by this method are compared with results obtained by other procedures.

It is possible, but not advisable, to determine the solubility by a simple procedure in which the measured potential of a saturated amalgam is combined with the Nernst equation. The method described above for determining the solubility from a plot of E against log C is more reliable and precise.

Other electrochemical methods, based on the oxidation of the metal from the amalgam electrodes being studied, may also be used, but such experiments should be carefully performed to obtain results which may be unequivocally interpreted.

Theoretically, such methods as amalgam polarography or chronopotentiometric or voltammetric oxidations of amalgams may be used. In practice, difficulties may arise due to relatively fast dissolution of crystals of the metal being oxidized when the concentration of that metal at the interface drops to zero. If the rate of this dissolution is appreciable, the recorded currents (or, in chronopotentiometry, the transition times) will be larger than they should be on the basis of the actual concentration of the saturated amalgam, which is to say that the concentration of saturated amalgams calculated from the measured current or transition time would be too large. This effect should be rather small in amalgam polarography, for a two-phase amalgam placed in the amalgam reservoir tends to separate, usually yielding an upper layer containing the metal crystals (if, as is true for many metals, the density of the metal being investigated is lower than that of mercury), together with a lower phase consisting of the saturated amalgam that will flow through the capillary into the electrolytic cell.

In other techniques, however, where the heterogeneous amalgam is prepared and used *in situ*, as for instance in the electroreduction of metal ions and subsequent re-oxidation of the metal at the hanging mercury-drop electrode (HMDE), the dissolution of metal may influence the determination of solubility.

TABLE 1

Solubilities of Some Metals in Mercury[6]

	Solubility (atom percent)			
Metal	Determined by potentiometric method		Determined by other methods	
Indium	68.3	(4)	70.3	(15)
	68.0	(5)		
Thallium	42.6	(7)	43.7	(16)
Tin	1.26	(9)		(17, 23)
	1.27	(10)	1.2	
	1.10	(11)		
Zinc	5.6	(3)	5.83	(18)
	6.4	(12)	6.4	(19)
Bismuth	1.2	(1)		
	1.1	(13)	1.4	(19)
Copper	8×10^{-3}	(3)		
	9×10^{-3}	(5)	1.0×10^{-3}	(20)
Lead	1.2	(3)	1.6	(21)
	1.1	(14)		
			4.7×10^{-3}	(6)
Manganese	6.6×10^{-3}	(3)	9.5×10^{-3}	(22)
			6.5×10^{-3}	(23)
			4.8×10^{-3}	(24)
Antimony	3.8×10^{-4}	(8)	1.1×10^{-3}	(25)
	4×10^{-4}	(8)	3.8×10^{-4}	(8)

References are given in parentheses.

This method will be discussed in greater detail, taking as an example the determination of solubility of manganese in mercury, which has been studied by several workers.

Sagadieva[26] used amalgam polarography and found the solubility to be 2.64×10^{-3} wt% at 17°C. Kemula and Galus,[27] using voltammetry with linearly varying potential with hanging amalgam-drop electrodes filled with heterogeneous manganese amalgam, found 1.26×10^{-3}%.

Because the anodic peak was not well developed, the concentration of the saturated amalgam was calculated by measuring the total charge consumed in the oxidation of manganese from the amalgam drop. This charge was related to the volume of the drop. A practically identical result was later obtained by Krasnova and Zebreva,[28] who also applied the HMDE on which manganese was deposited from solutions containing different concentrations of manganese (II) ions. The amalgam formed by electroreduction under identical conditions was subsequently oxidized, and the anodic peak current was plotted against the concentration of manganese. The dependence is linear at low concentrations of manganese, but at higher concentrations the peak current was not much dependent on concentration and was also much less reproducible. According to the authors, the phenomena are due to appearance of the solid phase in the system. They assume that the result [$(1.2 \pm 0.4) \times 10^{-3}$ w %] could be influenced to some extent by the displacement of the equilibrium between the liquid and solid phases and also by the self-dissolution of manganese due to its reaction with water, which has already been reported.[3,23]

The dissolution of manganese in mercury was also studied extensively, using the voltammetric method, by Kozlovskii and co-workers.[29] These investigations were carried out over a wide range of temperatures, from 20 to 95°C.

The solubility was determined by plotting the limiting oxidation current at −1.1 V against the concentration of manganese in the amalgam-pool electrode. Typical plots taken from their paper are shown in Figure 2. The solubility was determined from the intersection of two straight lines drawn through the experimental points. The data, obtained together with earlier data of these authors[30] for temperatures from 20 to 50°, are shown in Figure 3. The solubility increases linearly with increasing temperature up to approximately 80°C. At higher temperatures, another linear dependence is obtained but with a considerably higher slope. This change is attributed by the authors to a transformation occurring in the solid phase that is in equilibrium with the saturated amalgam. It is well-known[31-33] that up to 75°C. solid manganese amalgam exists as the intermetallic compound Mn_2Hg_5, but that at 75°C this compound decomposes to MnHg, which is stable up to 265°C.[31] This means that up to 75°C the solubility is determined by Mn_2Hg_5 and at higher temperatures by MnHg, and the change of slope of course reflects the difference between the enthalpies of solution of these compounds.

Such voltammetric methods for the determination of solubilities have the same limitations as other methods. If the metal is poorly soluble in mercury, the current obtained for its oxidation from the amalgam may be too small for convenient and accurate measurement in the presence of the capacity current and currents due to side reactions. It seems that in such a case the use of a square-wave or pulse technique, which provides significant rejection of the capacity current, should shift the limit of application of the method. Such work could be carried out in the future with some transition metals that are only slightly soluble in mercury.

At the other extreme, such determinations of the solubilities of metals that are freely soluble in mercury will give results that are too high because then the dissolution of solid metal in the time of oxidation of the homogeneous amalgam may be important. In such a case, the solid phase should be separated from the saturated amalgam before the concentration of the metal in the latter is determined. However, this greatly complicates the procedure and is likely to give rise to doubt as to whether the separation was complete. The optimum range of concentrations seems to be between 10^{-5} and 10^{-2} *M*.

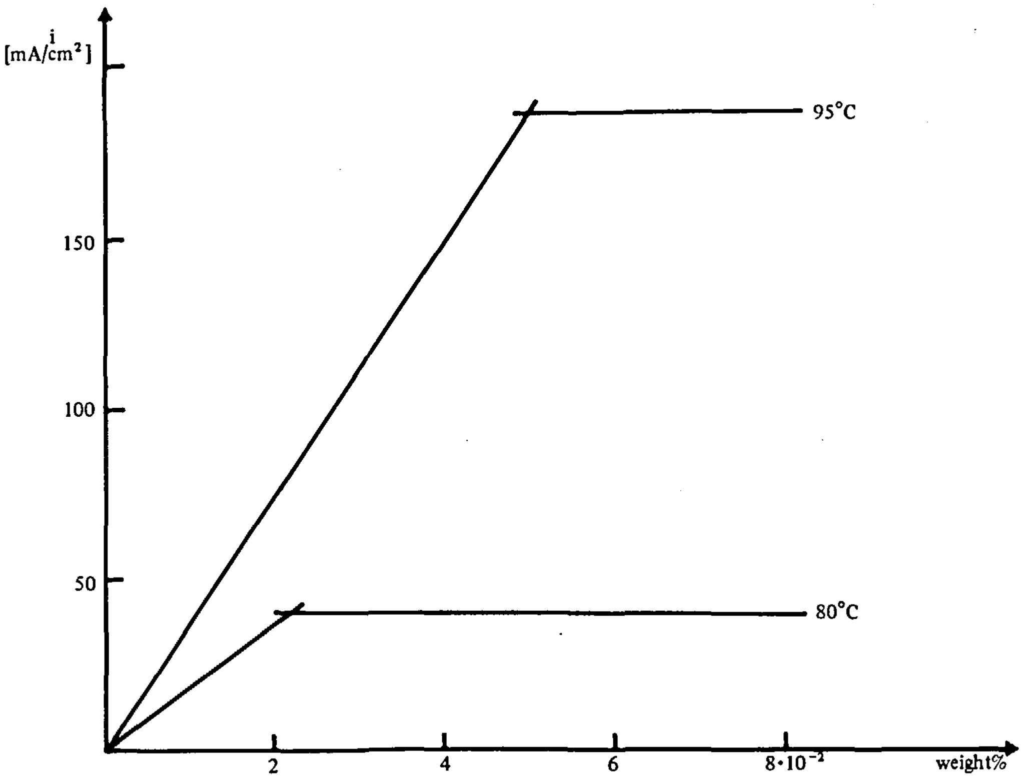

FIGURE 2. Dependence of limiting current for the oxidation of a manganese amalgam on the concentration of the amalgam. The temperature of the electrolytic cell is given beside each curve.[29]

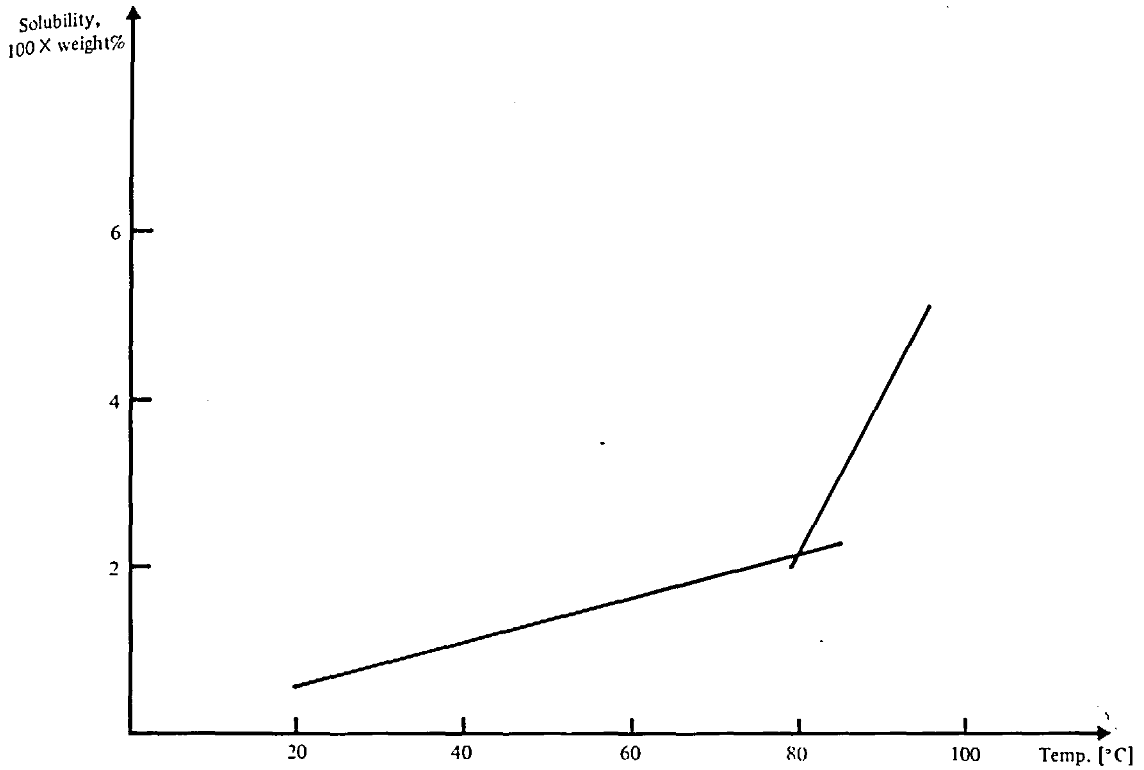

FIGURE 3. Dependence of the solubility of manganese in mercury on temperature.

1.2. Electrochemical Studies of the Kinetics and Mechanisms of Dissolution of Some Metals in Mercury

The problem of the kinetics of dissolution of metals in mercury has not been sufficiently studied even up to this day. It is especially striking to compare the few investigations that have been made with the far more numerous ones dealing with the dissolution of solid substances in aqueous or non-aqueous solvents.

Although electrochemical methods often do not play a principal role in such studies, their results are discussed briefly here for the sake of a more complete treatment of the electrochemical investigations of amalgams.

Bennet and Lewis[34] investigated the rates of dissolution of bismuth, lead, tin, and zinc in mercury. These metals were placed in vessels filled with mercury which were rotated to provide uniform rates of mass transport and dissolution.

After dissolution in this way for a prescribed time the amalgam was analyzed to find the concentration of dissolved metal. It was found that tin and lead dissolve more uniformly in mercury than bismuth does, and that smooth surfaces were not obtained when large crystals of zinc were partially dissolved. Investigations of zinc samples etched with acid before and after dissolution for some time revealed that this irregular dissolution depends on the grain structure; some experiments were also performed with zinc crystals of known orientation.

The final results and their analysis showed that, within the limitations of the experiments, the dissolution rates of tin and lead were controlled by mass-transport alone, whereas the rate of dissolution of zinc was partly controlled by the chemical step, for which the rate constant was found to be 5×10^{-4} cm s^{-1} at 30° and 8.3×10^{-4} cm s^{-1} at 40°. These are the mean values for all faces of the crystal. The activation energy of the chemical process is approximately equal to 10 kcal $mole^{-1}$.

The rates of dissolution of solid polycrystalline zinc, silver, and tin in liquid mercury have also been studied under turbulent flow conditions (rotating solid cylinders with and without simultaneous ultrasonic fields) by Hinzer and Stevenson.[35] These studies were carried out at different temperatures using radioactive traces to follow the reaction. Single crystals of zinc and a zinc-mercury intermediate phase were studied to gain further insight into the mechanism of dissolution. The rate constant was constant when ultrasonics were applied, but varied with concentration under pure rotation for all of the systems studied. The variation could not be explained by the dependence of diffusion coefficients on concentration. The solution rate constants were related to Reynolds and Schmidt numbers using dimensionless correlations.

The exponents on the Reynolds and Schmidt groups were found to be consistent with mass-transport control, except for the zinc-mercury system, which again appeared to be controlled by the rate of a chemical process as well as by that of mass transport, in agreement with earlier findings.

Experiments performed on single crystals of zinc showed that planes perpendicular to the basal plane dissolve more rapidly than the more densely packed basal planes. The rate of dissolution of zinc from the γ-intermediate phase (46 wt % Zn – 54% wt % Hg) was also studied.

The zinc-mercury phase diagram shows a peritectic reaction at 43° resulting in the formation of an intermediate γ-phase. Below 43° this phase is stable in the concentration range from 44 to 48 wt % of zinc. This intermediate phase could form at temperatures below 43° by reaction of mercury with the zinc samples. If this phase dissolves in mercury more slowly than zinc, it could act as a barrier and decrease the solution rate.

Since the flux of mass away from the interface is smaller toward the end of the solution process, the formation of intermediate phase by back-diffusion of mercury would be more likely to occur in the latter stages of solution. If this were the case, the decrease in the rate constant for dissolution toward the end of the experiment might be explained by the formation of the intermediate phase. In order to prove or disprove this possibility experimentally, the intermediate phase was prepared and its solution rate into mercury was studied.

The reaction was followed by observing the increase in activity of Zn^{65} in the liquid amalgam. Comparing the results with those for pure zinc under the same conditions, it is seen that the rate of dissolution of the intermediate phase in mercury is faster than the rate of dissolution of zinc in mercury. From this and other experiments it was concluded that the formation of the intermediate phase does not act as a barrier for the solution reaction and does not lower the rate of dissolution.

While the rate of dissolution of zinc in mercury is partly controlled by the rate of a chemical process, the rates of dissolution of tin and silver were found to be transport-controlled over the range of experimental conditions studied (temperatures from 3 to 59°C; rotation speeds of 200, 1300, and 4000 rpm).

The fact that the rate of dissolution is significantly lower for the basal plane than for the faces perpendicular to the basal plane was qualitatively explained by Hinzner and Stevenson[35] on the basis of the fact that nine nearest-neighbor bonds in the solid are broken in the former case as against seven or eight in the latter. This correlates with the higher heat of sublimation for the atoms in the former case.

In the foregoing papers the dissolved metals had the shape of cylinders. For the case in which a disc of metal is rotated in a liquid a precise theory of mass transport has been elaborated by Levich.[36]

Such rotating lead discs were dissolved in mercury in experiments carried out by Moshkievich and Ravdel.[37] Discs prepared from pure lead were polished and then mounted in Teflon.® The rate of rotation was varied from 25 to 3000 rpm. After a definite time of dissolution the lead disks were weighed.

It was found that in the range of temperatures from -35 to +50°C the rate of dissolution increases with the rotation rate (Figure 4), indicating that the process is controlled by the transport rate. A further increase of the rate of dissolution at higher rotation rates was explained as being due to the change of the flow from laminar to turbulent. Usually this change begins at

$$Re = \frac{r_0^2 \omega}{\nu} = 10^4 \qquad (1.2)$$

where Re is the Reynolds number, ν is the kinematic viscosity, r_0 is the radius of the disc and ω is the angular velocity of rotation.

Since the discs used in this work had diameters of 0.74 cm, one may expect the change from laminar to turbulent flow to occur at 750 to 800 rpm.

The dependence of the dissolution rate on the rate of rotation of the disc is lower than that calculated on the basis of Levich's equation

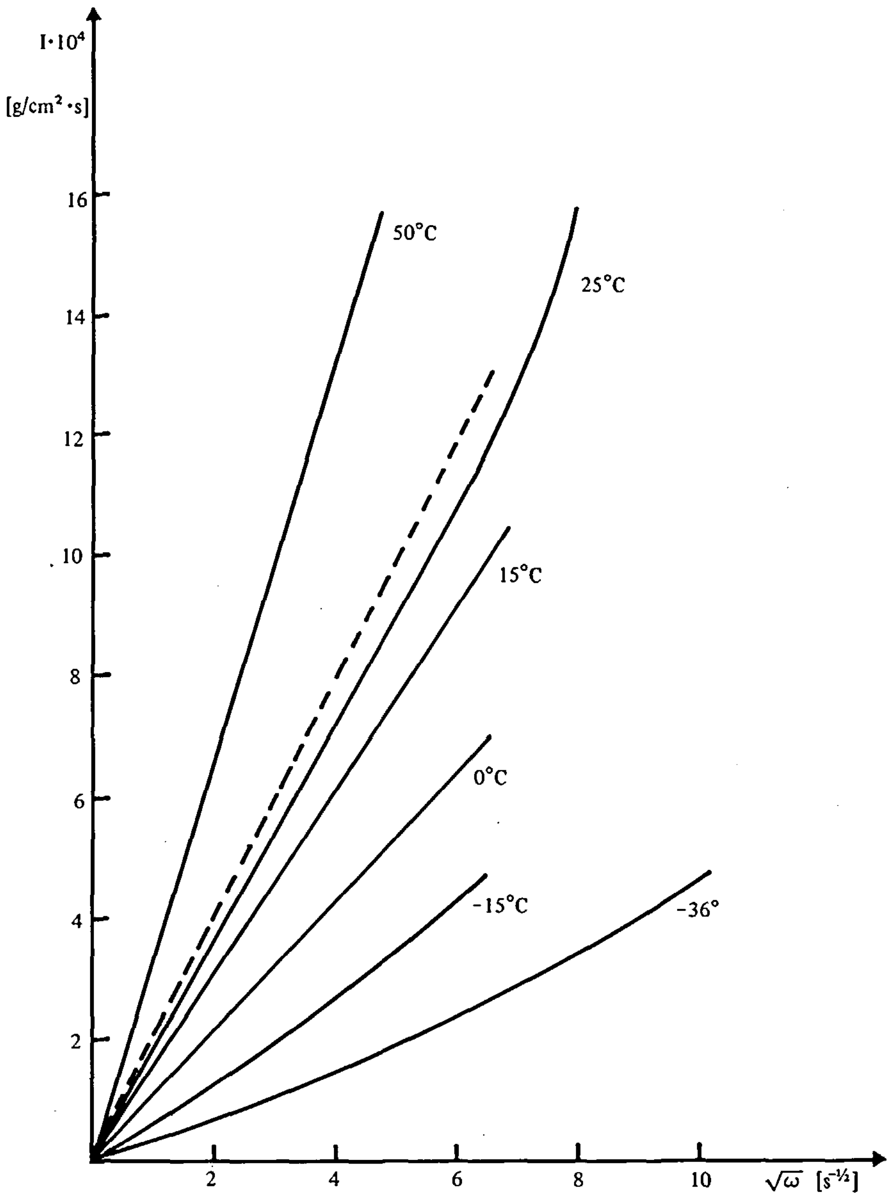

FIGURE 4. Dependence of the rate of dissolution of lead in mercury on the square root of the rate of rotation of the lead disc. The temperature of dissolution is given beside each curve.

describing the flux at disc electrodes. A correction was accordingly proposed to allow for the very low kinematic viscosity of mercury, but although the introduction of this correction diminishes the discrepancy between the calculated and experimental values it does not remove it completely.

The residual difference was ascribed to a dependence on concentration of the diffusion coefficient of lead in mercury phase and to the possibility that the values of diffusion coefficient of lead given in the literature are erroneously high. However, the value used in their calculations (1.16×10^{-5} cm^{2}s^{-1}) is the lowest one given in the literature, and its correctness is confirmed by our experiments (see Section 3). Assuming this value to be correct, one must conclude that there are some other reasons for the observed discrepancy.

Recently, Igolinski and Shalaevskaya[38] proposed a purely electrochemical method based on the application of the amalgam-film electrode. A thin layer of mercury covers some polished part of the metal investigated. The saturated amalgam then forms. On applying a sufficiently positive potential to the electrode in an appropriate circuit, the metal dissolved in this amalgam is oxidized, and a steady state is attained as a result of dissolution of metal at the metal-mercury interphase. Under chronoamperometric conditions, when the potential is sufficiently positive to keep surface concentration of the metal in amalgam equal to zero, the i-t curves will have the shape shown in Figure 5.

Assuming that the dissolution of the solid metal in mercury is described by a first-order kinetic equation, the authors derived the equation

$$\frac{nFA}{i} = \frac{i}{k'C_M} + \frac{h}{D_M C_M} \qquad (1.3)$$

where i is the current; D_M and C_M are the diffusion coefficient and concentration of the metal in the saturated amalgam, respectively; A is the true area of the surface of the amalgam at its boundary with the solution; k′ is the observed rate constant; and h is the thickness of the film of mercury.

Equation 1.3 shows that the overall rate of the process is governed by the rates of two separate steps: the dissolution of the solid phase, and the

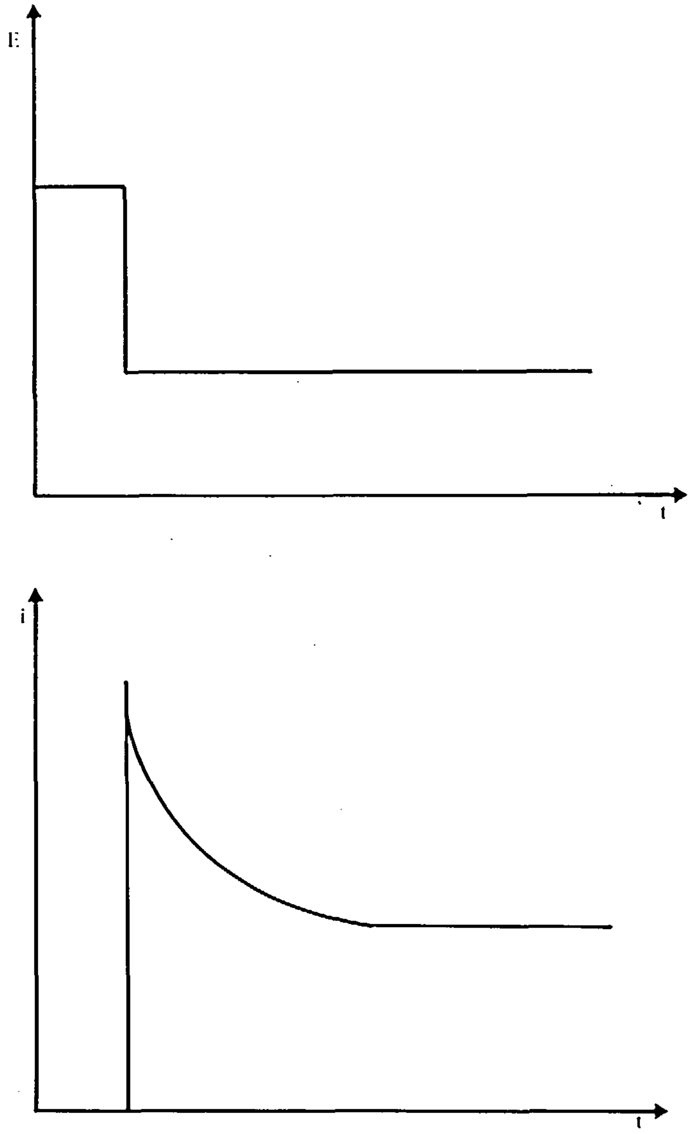

FIGURE 5. The lower curve shows the dependence on time of the current for the dissolution of a metal from a film electrode. The upper curve shows the change of potential in the same experiment.

diffusion of metal atoms through the mercury film to the mercury-solution interface. It follows from this equation that the dependence of nFA/i on h should be linear. This can be studied experimentally by preparing electrodes with films of different thickness. From the slope of a plot of nFA/i against h, the diffusion coefficient of the metal in mercury may be determined and the intercept of the line with the nFA/i axis (at h = 0) gives $1/k'C_M$. If the diffusion coefficient is known, evaluation of the slope and intercept enables one to determine both k′ and C_M. If this is done at different temperatures, one may construct a plot of log k′ against 1/T and obtain from it the energy of activation for the dissolution in mercury of the metal investigated.

This method was applied by Igolinski and Shalaevskaya[38] to the investigation of the dissolution of copper in mercury. The calculated values of the different parameters for that process are given in Table 2. The diffusion coefficients of copper in mercury were taken from the literature. The experimentally determined heat of melting of the solid phase which dissolves in mercury agrees very well with the heat of melting of pure copper, which is −3238 cal/mol. This suggests that the phase that dissolves under the non-equilibrium conditions of these experiments is copper itself, not the intermetallic copper-mercury compound that is in equilibrium with the saturated amalgam. Probably this compound does not form under non-equilibrium conditions.

Electrochemical methods are well suited for investigations of the mechanisms of dissolution of metals in mercury and should be more widely applied. It may be expected that new electrochemical procedures for study of dissolution will be developed in the future.

1.3. The Formation of Dispersed Metal Crystals During Electroreductions of Metal Ions at Mercury Electrodes

It has already been said that an amalgam of the reduced metal is very often formed during the electroreduction of metal ions to the metallic state at mercury electrodes. However, it has sometimes been observed that the deposited metal does not enter into the mercury phase, but remains on the surface of the electrode, where it often forms a finely divided precipitate. One should add that such behavior has been observed both for metals that are sparingly soluble and for metals that are highly soluble in mercury.

In other experiments a reduced metal that is sparingly soluble in mercury but enters into the mercury phase has been found to remain there as finely divided particles, and large crystals are not formed.

In still others, the electroreduction of a metal ion at an amalgam electrode produces an intermetallic compound between the metal originally present in the amalgam and that formed in the process of electroreduction. Such intermetallic compounds also remain as finely divided particles in the mercury.

These observations may be important from the technical point of view as they give a way of preparing metal powders.

Various explanations have been advanced to account for the formation of dispersed metallic precipitates. They have involved the low solubilities of metals in mercury,[39–41] the supersaturation of the surface layer of mercury,[42] the effect of amalgam formation on the surface tension,[43] or a rate of deposition that exceeds the rate of transport metal into the bulk of the mercury.[44,45]

However, the problem has not been studied

TABLE 2

Parameters for the Dissolution of Copper in Mercury

Temperature (°C)	$D \times 10^5$ ($cm^2\ s^{-1}$)	$C_M \times 10^5$ ($mol\ cm^{-3}$)	$k' \times 10^3$ ($cm\ s^{-1}$)	Activation energy ($cal\ mol^{-1}$)	Heat of melting ($cal\ mol^{-1}$)
22	0.89	2.22	3.40		
30	1.05	2.50	4.42		
40	1.22	2.73	5.81	4635	3240
50	1.28	3.33	7.00		
60	1.34	4.00	8.33		
70	1.50	4.57	10.94		

systematically. Only recently has there been an attempt[46] to explain the mechanism of formation of such precipitates and to describe more precisely the conditions under which they form. It was concluded that the formation of such precipitates at the electrode surface does not depend on the solubility of the deposited metal, for even such metals as indium and thallium, which are extremely soluble in mercury, may form precipitates, as had already been observed by Calusaru and Kůta.[47] It was also concluded that the formation of such precipitates is unrelated to the surface tensions of the amalgams involved.

Such precipitates form at potentials so negative that the concentration of the metal ions is significantly decreased at the electrode surface. Especially interesting were experiments which showed that, at constant current density, crystallization is facilitated by diluting the solution.

To explain their experiments, these authors assume that the metal crystallites form, not on the electrode surface, but at some distance from it. It is preceded by the formation of zero-valent complexes at the electrode surface; according to Geinrikhs et al.,[46] these may diffuse away from the electrode surface and eventually give rise to nuclei by collision. When this precipitate comes into contact with the electrode, the dispersed precipitate develops on these microcrystals. Their dimensions must be such that the crystals grow more rapidly toward the solution than they dissolve in the mercury.

However, it should be stressed that the problem is very complicated. From the information available, one may conclude that reduced metals ought to be wetted by mercury. There are at least two phenomena that, by hindering that process, may enhance the formation of dispersed precipitate at the electrode surface(!). One is the passivation of the deposited metal by the formation of a layer of oxide or some other substance. For instance, cobalt(II), when reduced from many solutions at mercury electrodes, is amalgamated and enters into the mercury phase. However, its reduction from thiocyanate solutions results in the formation of metallic cobalt[48] on the surface of the mercury electrode because of the simultaneous reduction of thiocyanate ions to sulfide ions and the resulting formation of CoS at the electrode surface; the adsorption of this precipitate onto the electrode surface may inhibit the wetting of the deposited cobalt by mercury. Similar behavior under certain conditions has also been observed[49] for electroreduction of nickel(II) from thiocyanate solutions.

A second phenomenon which may protect the metal against being wetted by mercury and prevent its entrance into the mercury phase results from the presence of surface-active compounds in the solution investigated. Barański,[50] in the laboratory, could repeat the results obtained by Calusaru and Kůta[47] for the reductions of O, 1*M* Tl(I), Pb(II), and Cd(II) only after adding significant concentrations of gelatin to the solutions. When this was done, even the reduction of mercury(II) at mercury electrodes gave rise to small drops of mercury at the surface of the electrode.

One may imagine that, when the electrode surface is blocked by a surface-active substance, tunneling of electrons through the adsorbed layer occurs at negative potentials, and the metallic precipitate develops at some distance from the electrode surface. The formation, during the electroreduction process, of finely dispersed particles of metals sparingly soluble in mercury may also indicate that in the absence of passivation, microcrystals which form at the electrode-electrolyte interface are wetted and the formation of new microcrystals begins.

This section has presented some experimental results and some views, but the problem with which it deals is one on which much work remains to be done.

1.4. Oxidation of Heterogeneous Amalgams

The oxidation of a heterogeneous amalgam can frequently be effected by applying a sufficiently positive potential to an electrode made from the amalgam being investigated. However, there is more to the matter than meets the eye, for the oxidation may be dependent on the way in which the amalgam was prepared (*in situ* with fast oxidation, or outside the cell in which the electrooxidation is carried out) and also on the way in which it is oxidized (from dropping or stationary amalgam electrodes).

Kozlovskii and Zebreva[51] assume that metals sparingly soluble in mercury are oxidizable only if they are deposited onto the surface. According to them, amalgamation protects any metal that is present in mercury as a second phase against oxidation. This is probably true if the oxidation is carried out under polarographic conditions, because then the drop time may appear to be insufficiently long for metal particles to reach the surface of the amalgam. Moreover, in amalgam polarography with heterogeneous amalgams, there always exists the possibility that the solid particles of metal will not be uniformly distributed throughout the mercury phase: there may be more particles per unit volume of amalgam in the upper part of the amalgam (i.e., in the reservoir) than there are at the bottom.

The oxidation of heterogeneous amalgams was investigated by Jangg and co-workers.[52] These authors studied the oxidations of several heterogeneous amalgams containing only a single metal (iron, cobalt, nickel, copper, or manganese) and also those of some complex heterogeneous amalgams containing, for instance, iron and cobalt, or manganese and iron. Oxidation was observed, in solutions of chlorides and sulfates, at potentials close to those at which mercury is oxidized.

According to the mechanism elaborated by these workers, the process has to be initiated by the oxidation of mercury. The charge is then partially transferred to microcrystals of the metal which are suspended in the amalgam. On acquiring this charge, these particles lose their metallic character, become partly ionized, and as a result are not so well wetted by mercury as before. This decrease of wetting is responsible for the transfer of microcrystals from the bulk of the amalgam to its surface where the electrooxidation may proceed.

This mechanism is not well-founded and the proposed partial ionization of the microcrystals is not well-understood. It is also by no means certain that oxidation of mercury must precede the oxidation of a heterogeneous amalgam.

Barański[50] has proposed another mechanism. He assumed that in a heterogeneous amalgam, though the solid microcrystals are well wetted by mercury, there are always some centers at which the surfaces of some microcrystals are in indirect contact with the solution. These centers may form or disappear as a result of fluctuations.

If a sufficiently positive potential is applied to such an amalgam, the oxidation will proceed mainly on these centers, and the local current density in a galvanostatic experiment will reach a high value. As a result, the centers may be passivated. The change of the surface energy at the three-phase boundary thus produced may lead to an increase of the surface area of the non-wetted regions, and this deamalgamation may facilitate the oxidation of the metal (e.g., cobalt) at the surface of the electrode.

This mechanism of oxidation of heterogeneous amalgams may be valid if there is a rather large amount of the solid phase that is not very far from the mercury surface. Otherwise, the mechanism may be very simple, consisting of the dissolution of the solid phase prior to the oxidation. However, although this seems quite probable if the metal is relatively soluble in mercury, it would not be sufficiently efficient if the solubility of the metal is very low.

1.5. Electrochemical Investigations of Some Simple Amalgams

It is convenient to discuss the properties of amalgam on the basis of the periodic table. From this point of view, all metal amalgams may be divided into the following four groups:

a. amalgams of the alkali and alkaline earth metals,
b. amalgams of f-group metals,
c. amalgams of p-group metals, and
d. transition metal amalgams.

Both the f- and the s-group metals form a number of intermetallic compounds with mercury.

Metals of the p-group interact weakly with mercury, and usually give rise to homogeneous amalgams that are in equilibrium with either a solution of mercury in the metal or an intermetallic compound having a small enthalpy of formation.

Probably the most interesting amalgams are those formed by transition metals. Usually these have low solubilities in mercury, and some of them form intermetallic compounds with mercury. Not all of the properties of these amalgams are known, and further investigations of them are needed. In the investigations that have been performed, electrochemical methods have played the important role. This short review of the topic will therefore begin by discussing investigations of some amalgams of this group. First place belongs to amalgams of the platinum-group metals, which are very interesting because they contain several intermetallic compounds with mercury.

1.5.1. Platinum-group-metal Amalgams

1.5.1.1. Nickel Amalgam

Early investigations, carried out by various methods, revealed the formation of intermetallic compounds in the nickel-mercury system. Brill and Haag[53] found the formation of $NiHg_3$ roentgenographically. Lihl[54] postulated the existence of an intermetallic compound with a composition changing from $NiHg_3$ to $NiHg_4$. Lihl and Nowotny[56] found that the structure of $NiHg_4$ is analogous to that of $PtHg_4$. Bates and Prentice,[55] by measuring magnetic susceptibility, found heterogeneous nickel amalgams to be diamagnetic but to become ferromagnetic after heating to 220°C. This was explained as due to the decomposition of intermetallic compounds and the appearance of metallic nickel in the system. Similar observations were reported by Pavlek.[32]

Jangg and Steppan[57] have measured the dependence of the vapor pressure of mercury on the composition of nickel amalgam and confirmed the formation of $NiHg_4$, which on heating decomposes directly with formation of metallic nickel (at 232°C at normal pressure). They also determined the thermodynamic parameters for the formation of this compound.

A number of investigations have also been carried out to determine the solubility of nickel in mercury. All these studies point to a low solubility, of the order of 10^{-5} atom percent. It should be said, however, that there has as yet been no determination of the composition of the solid phase which should remain in equilibrium with the amalgam.

Though the solubility of nickel in mercury is very low, Kemula and Galus[58] found that it is possible to prepare supersaturated nickel amalgams by the electroreduction of nickel(II) at mercury electrodes. One may obtain even 10^{-3} *M* amalgam. The stability of the supersaturated amalgam was investigated later by Galus,[59] using current-reversal chronopotentiometry. Such amalgams were found to be unstable and to undergo transformation into intermetallic compounds. Nickel amalgam was also investigated electrochemically by Krasnova and Zebreva.[60]

The stability of nickel amalgam, its anodic behavior, and the equilibria existing in the nickel-mercury system were recently investigated by Barański and Galus.[61] The electrochemical behavior was initially investigated by using cyclic voltammetry. Figure 6 shows the cyclic voltammograms of nickel at various concentrations recorded with an HMDE in a 6 *M* aqueous solution of calcium chloride. Curve a of this figure shows an almost reversible behavior, typical of the dilute homogeneous nickel amalgam in this medium. Similar curves were recorded at higher temperatures in 5 *M* solutions of glycerine containing lithium chloride.

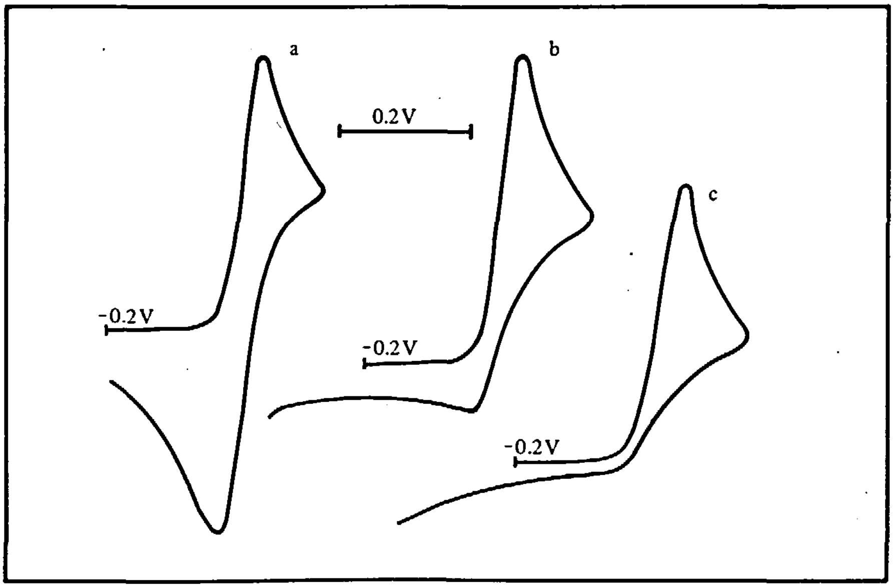

FIGURE 6. Cyclic voltammogram curves of nickel in 6 *M* $CaCl_2$, obtained with the use of the HMDE at 20°C. The scan rate was 1.5 V min^{-1} and the concentration of nickel(II) was (a) 10^{-3} *M*, (b) 2×10^{-3} *M*, and (c) 4×10^{-3} *M*. Potentials are referred to the S.C.E.

Curve a of Figure 7 shows the cyclic voltammogram of nickel recorded at 229°C. An increase of the concentration of nickel(II) in the solution leads to the disappearance of the anodic peak. However, a small and slightly potential-dependent anodic current is still observed (Figure 6, curve c). The anodic behavior at higher concentrations of nickel depends to a large extent on temperature, as follows from a comparison of curve c in Figure 6 with curve b in Figure 7.

A voltammetric study of the electroreduction of nickel(II) and 0.01 *M* to 0.10 *M* mercury(II) has been carried out at a platinum electrode from stirred 6 *M* aqueous solutions of calcium chloride over the range of temperatures from 20 to 60°C. Below 40°C, current-potential curves were smooth and highly reproducible and had surprisingly well-defined limiting currents, probably because of the high viscosity of the supporting electrolyte.

Figure 8 shows the curves obtained with a solution containing 0.1 *M* mercury(II) and nickel(II). In the range of potentials in which nickel(II) ions are electroreduced, two waves are observed; their half-wave potentials are -0.40 and -0.56 V. The ratio of the height of the wave at -0.40 V to the height of the mercury(II) wave was always very close to 1/3, and was independent of

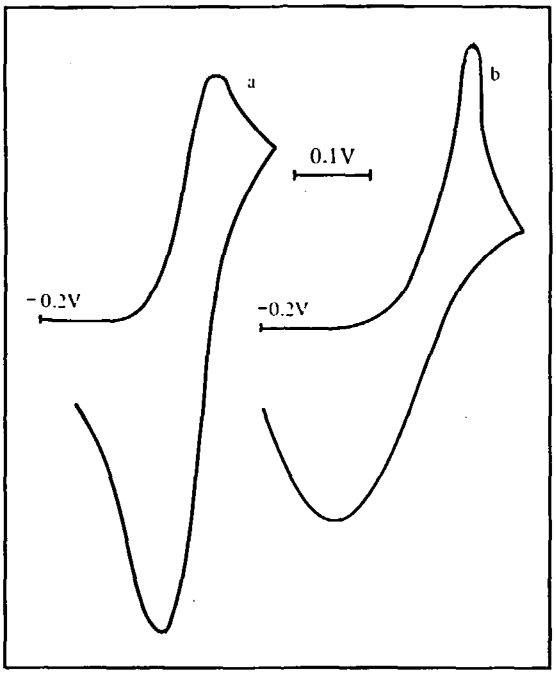

FIGURE 7. Cyclic voltammogram curves of nickel in 5 *M* LiCl in glycerine, obtained with the use of the HMDE at 229°C. The scan rate was 0.4 V $\min^{-1}$ and the concentration of nickel(II) was (a) 5×10^{-3} *M* and (b) 5×10^{-2} *M*. Potentials are referred to an internal $Ni^{2+}/Ni(s)$ electrode.

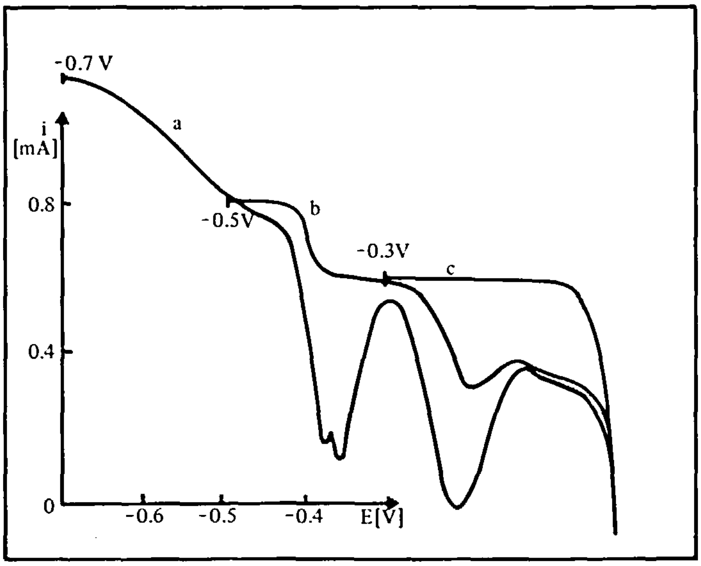

FIGURE 8. Voltammograms for the simultaneous electroreduction of nickel(II) and mercury(II) at the platinum electrode from a solution containing 0.1 *M* Ni(II) and 0.1 *M* Hg(II) in 6 *M* $CaCl_2$. The electrode area was 0.08 cm^2, the temperature was 20°C, and the scan rate was 0.4 V $\min^{-1}$. The starting potential was (a) -0.7 V, (b) -0.50V, and (c) -0.3 V vs. S.C.E. The solutions were mixed with a magnetic stirrer during the experiments.

the concentrations of the two ions in the solution, if the excess of nickel(II) in the solution was sufficiently large. The sum of the heights of the waves at −0.40 and −0.56 V is linearly dependent on the concentration of nickel(II) in the solution. The first double anodic peak, occurrring at a potential of −0.35 V, is related to the second cathodic wave; it does not appear if the ratio of the nickel(II) to mercury(II) concentrations is lower than 1/3 or if the starting potential is more positive than −0.5 V (curve b in Figure 8).

The second anodic peak, occurring at −0.2 V, and the poorly defined peak at −0.10 to −0.15 V, are related to the first wave for the electroreduction of nickel(II) (curves b and c of Figure 8).

All these observations may be easily explained on the basis of the explanation advanced by Kemula and Galus,[5 8] which is that a supersaturated nickel amalgam is formed at first and then crystallizes into intermetallic compounds after reaching some critical concentrations.

Since the compounds $NiHg_4$ and $NiHg_3$ could be prepared without excess of nickel, it was possible to measure the equilibrium potentials of the systems $Ni^{2+}/NiHg_4(s)$, Hg and $Ni^{2+}/NiHg_3(s)$, Hg. The temperature dependences of these potentials were evaluated (Figure 9), and the enthalpy and entropy of formation of these compounds as well as their solubilities in mercury were calculated and are given in Tables 3 and 4. As may be seen from Figure 9, at temperatures below 60°C the potentials of the heterogeneous amalgams are intermediate between those of $NiHg_3$ and Ni(s). Since the equilibrium potentials were independent of the conditions under which the heterogeneous amalgams were formed, this lowering of the potential cannot be attributed to differences between the sizes or orientations of $NiHg_3$ crystals.

One may conclude that these potentials are determined by the new intermetallic compound $NiHg_2$. To prove this assumption, a roentgenographic study of a fresh amalgam containing 3 percent by weight of nickel was carried out, but it did not give a definite result because of interference by the excess of mercury in the samples investigated, indicating that $NiHg_2$ may exist only in admixture with $NiHg_3$. The former has a tetragonal structure, but it could not be prepared in a pure state and analytical confirmation of its composition was not possible. However, by analogy with the Pt-Hg system, one may assume that it has the composition $NiHg_2$, since $PtHg_2$ also has tetragonal structure and similar lattice constants. The enthalpy and entropy of formation of the postulated $NiHg_2$ were calculated on the assumption that this compound determines the potential at which nickel is reduced at the HMDE below 60°C.

At temperatures between 60 and 170°C, the main product of crystallization of the homogeneous nickel amalgam is $NiHg_3$. A parallel but much slower process leads to the formation of $NiHg_2$.

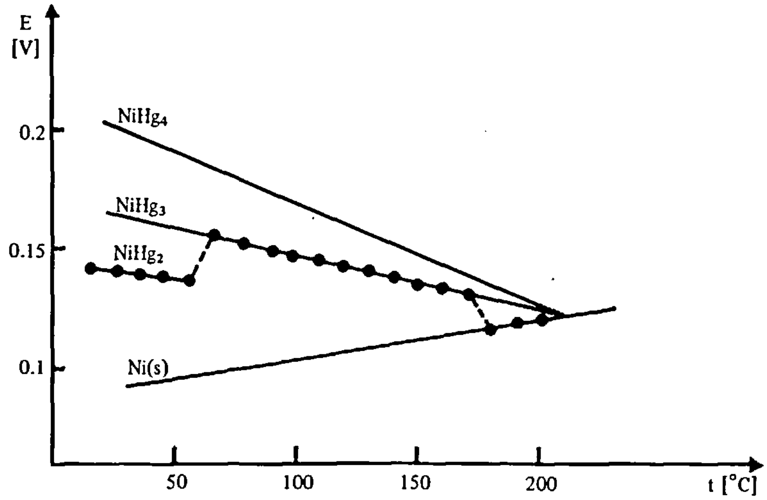

FIGURE 9. The dependences on temperature of the equilibrium potentials of various nickel-mercury compounds. "•••" = potentials of the HMDE after formation of heterogeneous nickel amalgam by electroreduction with a current of 0.2 mA for 30 s. Potentials are referred to a hypothetical homogeneous 1 *M* nickel amalgam electrode.

TABLE 3

Thermodynamic Parameters for Nickel-mercury Compounds[61]

Compound	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔG_{298K} (kcal mol^{-1})	Temperature (°C) and product of decomposition	Structure of the solid phase
$NiHg_4$	−13.1 ± 0.3	−27.0 ± 1	−5.04 ± 0.1	212 (Ni_s)	Reg. a = 3.002Å[54]
	−13.5 ± 0.5*	–	–	230 (Ni_s)	
	−12.6 ± 0.5[57]	−25.0 ± 1[57]	−5.19[57]	232 (Ni_s)[57]	
				220 (Ni_s)[55]	
$NiHg_3$	− 8.5 ± 0.3	−17.6 ± 1	−3.26 ± 0.1	210 (Ni_s)	Reg. a = 3.00Å[54]
$NiHg_2$	− 6.25 ± 1	−14.0 ± 3	−2.16 ± 0.1	185 (Ni_s)	Tetragonal a = 4.56 Å c = 2.83 Å
Homogeneous amalgam	+ 2.1 ± 0.3	− 7.2 ± 1	+4.24 ± 0.1	–	–

*From derivatographic measurements.

$NiHg_4$ is formed as well, but only very slowly. Its rate of formation may be greatly increased by introducing a dispersion of $NiHg_4$ into the mercury, showing that the formation of nuclei for the crystallization of a new phase is a rate-determining step. Since this is so, $NiHg_3$ and $NiHg_4$ should exist as individual phases, instead of forming a solid solution as was suggested by Lihl.[54]

The preference for the formation of solid $NiHg_3$ may result from the existence of that compound in the homogeneous amalgam. Such a possibility is also indicated by the low value of the diffusion coefficient of nickel in mercury. This problem will be discussed in Section 3.3.

Table 4 gives the solubilities of several intermetallic compounds of nickel with mercury, and compares them with the results of other workers. In the range of temperatures (above 212°C) where the formation of solid compounds is not possible, the solubilities by Barański and Galus agree well with those reported by Jangg and Pallman. At lower temperatures, the results of the latter workers are higher than the solubilities of the nickel-mercury compounds and lower than the solubility of free nickel. One may doubt whether true equilibrium between the liquid and solid phases was attained in their experiments especially since the rates of recrystallization in two-phase nickel amalgams are very low.

1.5.1.2. Palladium Amalgam

The early roentgenographic and magnetochemical investigations of Bittner and Nowotny[64] showed that the compounds Pd_2Hg_5 and PdHg are formed in the palladium-mercury system. Ubbelohde[65] pointed out the formation of the compound $PdHg_3$. More detailed investigations of the system have been carried out by Jangg and Gröll,[66] who obtained a phase diagram on the basis of thermal analysis. It follows from this study that, in addition to the compounds PdHg and Pd_2Hg_5 found by Bittner and Nowotny, there exists a third compound, $PdHg_4$, which decomposes at 90°C with the formation of Pd_2Hg_5 and mercury. Subsequently, Pd_2Hg_5 dissociates into PdHg and mercury at 238°C and PdHg is stable even at 500°C.

The solubility of palladium in mercury is quite limited and equal to only 5.1×10^{-3} atom percent.

There are almost no published electrochemical investigations of the palladium-mercury system. A recent study of it has been made by Kryska[67] in the writer's laboratory.

Since the potential of the Pd(II)/Pd(0) system and the potentials of oxidation of the intermetallic palladium-mercury compounds are quite positive, investigations were carried out using carbon-paste electrodes prepared by the procedure given by Adams.[68] Platinum electrodes were also used in some experiments. Palladium amalgam was obtained by the simultaneous electroreduction of palladium(II) and mercury(II) ions from saturated aqueous solutions of sodium bromide.

TABLE 4

Solubilities in Mercury of Intermetallic Nickel-mercury Compounds and Some Metals

Metal	Phase which determines solubility	Solubility (atom percent)									Literature
		20°C	50°C	100°C	150°C	200°C	300°C	400°C	500°C	550°C	
Ni	$NiHg_4$	1.5×10^{-7}	1.8×10^{-6}	4.1×10^{-5}	4.7×10^{-4}	3×10^{-3}	–	–	–	–	61
	$NiHg_3$[a]	3.4×10^{-6}	1.9×10^{-5}	1.6×10^{-4}	9.3×10^{-4}	3.6×10^{-3}	–	–	–	–	61
	$NiHg_2$[a]	2.3×10^{-5}	8.5×10^{-5}	4.7×10^{-4}[c]	1.8×10^{-3}[c]	–	–	–	–	–	61
	Ni[b]	1.1×10^{-3}	1.6×10^{-3}	2.4×10^{-3}	3.3×10^{-3}	4.2×10^{-3}	6.1×10^{-3}[c]	8.1×10^{-3}[c]	9.8×10^{-3}[c]	–	61
	t > 220°C	5.1×10^{-5}	–	3.4×10^{-4}	–	1.7×10^{-3}	5.9×10^{-3}	1.5×10^{-2}	2.3×10^{-2}	–	62
	Ni										
	t < 220°C	$< 6.8 \times 10^{-6}$	–		–						11
	?										
Co	Co	$< 3.4 \times 10^{-6}$	–	–	–	–	–	–	6.8×10^{-5}	8.1×10^{-5}	62,11
Fe	Fe	5.4×10^{-6}	–	7×10^{-6}	–	1.1×10^{-5}	1.9×10^{-5}	4.0×10^{-5}	7.6×10^{-5}	–	63
Mn	?	3.6×10^{-3}	–	1.2×10^{-2}	–	0.36	1.4	3.2	6.6	7.6	62
Cr	Cr	$< 1.6 \times 10^{-6}$	–	–	–	–	–	–	2.7×10^{-4}	3.3×10^{-4}	62, 11

[a] No true equilibrium with homogeneous amalgam.
[b] Equilibrium with homogeneous amalgam at temperatures exceeding 212°C.
[c] By extrapolation.

Depending on the ratio of the concentrations of palladium(II) and mercury(II), the number of steps on anodic chronopotentiograms of the amalgams changed from 1 to 4. Four different processes were involved, and they are characterized by the following half-transition-time potentials: I – +6 mV; II – +50 mV; III – +125 mV; and IV – +360 mV. When the solution contained only mercury(II), only one step (I) corresponding to its oxidation was observed. For solutions in which the concentration of palladium was equal to or higher than that of mercury(II), only step IV was recorded. The oxidation of free metallic palladium also occurred at the potential of step I. When the concentration of palladium was lower than that of mercury, two or three oxidation steps were found, depending on the ratio of these concentrations.

Typical chronopotentiograms for the oxidation of amalgams obtained by deposition of both metals from solutions in which the ratios of palladium to mercury concentrations were equal to 0.25 and 1 are shown in Figure 10. Figure 11 shows how the composition of the solution affects the quantities of electricity consumed in the individual anodic steps. For these diagrams, the values of the parameter $Q_i/\Sigma Q_{ox}$ corresponding to the four different transitions reach the maximum values for solutions in which the ratio of concentrations of palladium(II) to mercury(II) is equal to 0:1 for step I, 1:4 for step II, 2:5 for step III, and 1:1 for step IV. As the palladium/mercury ratio approaches a value at which the charge transferred in any particular one of these steps reaches a maximum value, the charge transferred in the preceding step tends to zero.

In experiments carried out at 95°C, step II was never observed. This agrees with the conclusion, reported earlier by Jangg and Gröll,[66] that the

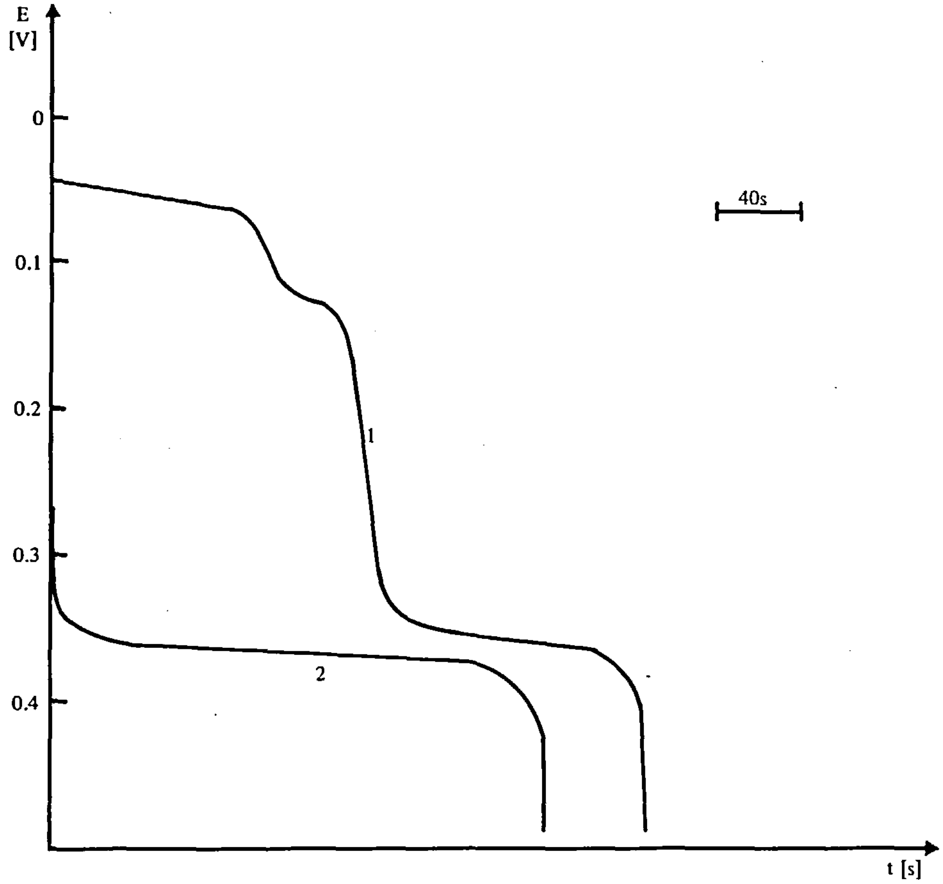

FIGURE 10. Chronopotentiograms for the oxidation of palladium-mercury compounds obtained by electrodeposition of palladium and mercury onto platinum electrodes. The ratio of concentrations, [Pd(II)]/[Hg(II)], in the solutions from which the deposition was carried out was (1) 1:4, (2) 1:1. The oxidations were carried out in saturated NaBr at 20°C. Potentials are referred to the $Hg/HgBr_4^{2-}$ (0.018 M), NaBr(s) electrode.

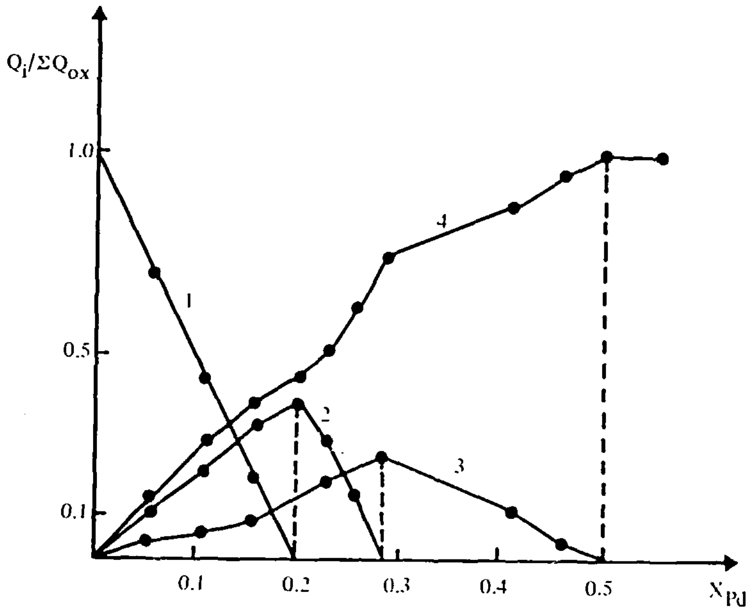

FIGURE 11. Dependence of $Q_i/\Sigma Q_{ox}$ on the composition of electrolyzed solution according to chronopotentiometric data obtained at 20°C with carbon-paste electrodes. Curve 1 corresponds to the oxidation of Hg, curve 2 to the oxidation of $PdHg_4$, curve 3 to the oxidation of Pd_2Hg_5, and curve 4 to the oxidation of PdHg.

compound $PdHg_4$ (whose oxidation is responsible for step II), does not exist at temperatures exceeding 90°C.

The character of the oxidation curves depends to a large extent on the current density used in the chronopotentiometric oxidation, both for the oxidation of Pd_2Hg_5 and for that of $PdHg_4$.

Stationary-electrode voltammograms show one or several peaks, depending on the amalgam composition. The shapes of these peaks depend on the scan rate.

The simultaneous electroreduction of palladium(II) and mercury(II) ions at carbon-pastes electrode was also studied by Kryska under potentiostatic conditions. The i-t curves showed maxima typical of electrocrystallization. As was expected, the times at which these maxima appeared were dependent on the potential of the electrode.

The dependence of current on time for the rising portions of the i-t curves may be described by the simple relation

$$i = k_k t^n \qquad (1.4)$$

where k_k is a proportionality constant dependent on the rate of the electrocrystallization. Plots of log i against log t were linear and their slopes corresponded to values of n close to 3.

The potentials of carbon-paste electrodes containing various deposited palladium-mercury compounds have been measured. Figure 12 shows how they depend on the composition of the solution from which mercury and palladium were deposited. There are three regions of concentration, each characterized by a constant value of the potential, and corresponding to the existences of different intermetallic compounds on the surface of the electrode.

The thermodynamic parameters of these compounds were evaluated from measurements made at temperatures from 20 to 95°C, and are given in Table 5. The accuracies of these values are not very high, because the reproducibility of measurement of the potential was limited by the comparatively low rates of the reactions that occur in this system.

The results of Jangg and Gröll were obtained from measurements of the vapor pressure of mercury in equilibrium with the solid intermetallic compounds. These authors did not give the parameters for the compound $PdHg_4$, and those given in Table 5 for that compound were calculated from potentiometric data for the reaction

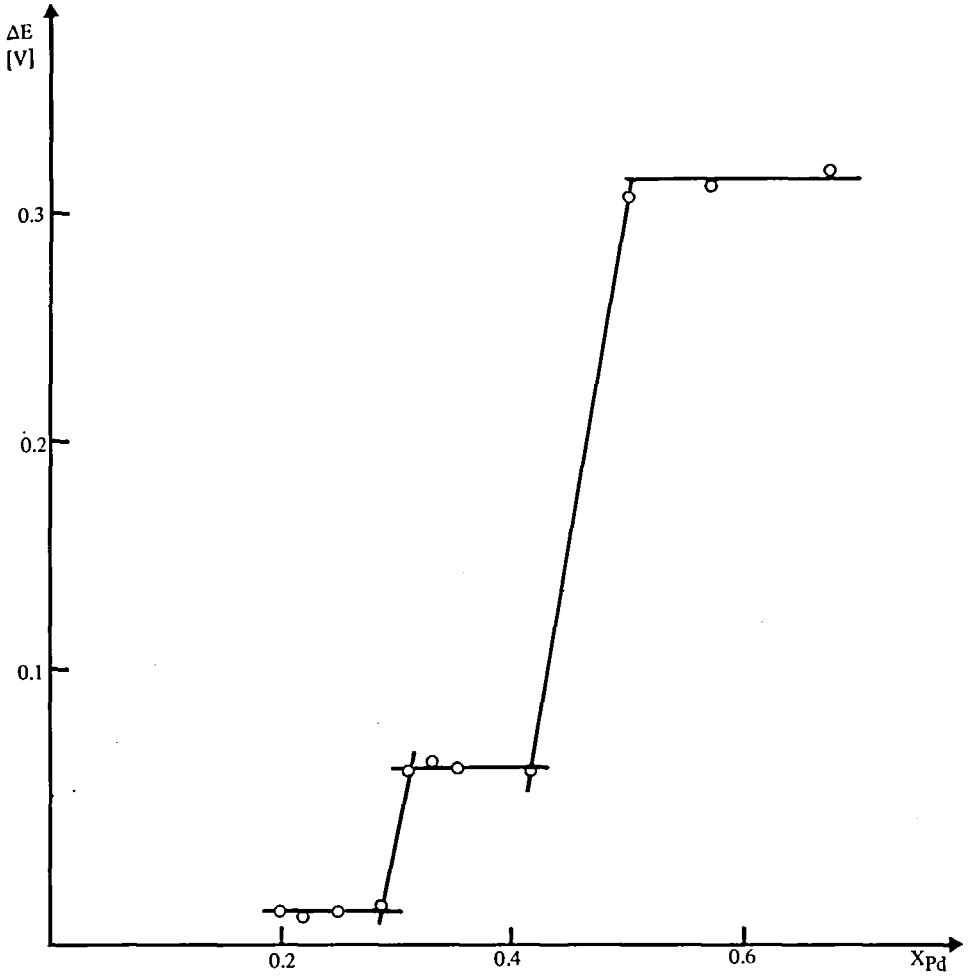

FIGURE 12. Dependence of equilibrium potentials of various intermetallic palladium-mercury compounds on the palladium content at 20°C. Reference electrode as in Figure 10.

TABLE 5

Thermodynamic Parameters for Several Palladium-mercury Compounds

Compound	ΔH (kcal mol^{-1})	ΔS (cal deg^{-1} mol^{-1})	ΔG_{298} (kcal mol^{-1})	Temperature of decomposition	Literature
PdHg	-21 ± 4.6	-22 ± 12	-14 ± 0.5	–	Kryska[67]
	-22.6 ± 0.8	-18 ± 1	-17.2	–	Jangg and Gröll[66]
Pd_2Hg_5	-61 ± 12	-88 ± 33	-35 ± 1	–	Kryska[67]
	-55.8 ± 1.5	-57 ± 2	-38.8	–	Jangg and Gröll[66]
$PdHg_4$	-31 ± 2	-38 ± 6	-20.1 ± 0.2	–	Kryska[67]

$$Pd_2Hg_5 + 3Hg \rightleftharpoons 2PdHg_4$$

together with parameters for the formation of Pd_2Hg_5 given by Jangg and Gröll.

The results obtained by Kryska suggest how the electrooxidation of palladium-mercury compounds occurs. The oxidation of $PdHg_4$ at low current density gives rise to three steps, of which the last two occur at the potentials where Pd_2Hg_5 and PdHg are oxidized, indicating that these compounds are formed and oxidized successively in a step wise process. Detailed studies showed that under these experimental conditions the oxidation proceeds not only on the surface of the electrode but practically throughout the entire volume of the amalgam.

When this oxidation is carried out at very high current densities, the slowness of the chemical steps that accompany the charge-transfer process becomes pronounced, and the oxidation curves are considerably changed.

1.5.1.3. Platinum Amalgam

Several intermetallic compounds may be formed in this system. They may be described as PtHg, $PtHg_2$, and $PtHg_4$, and they have been investigated by roentgenographic[71] measurements and by measurements of the vapor pressure of mercury.[57]

$PtHg_4$ has been considered to be the predominant product of the interaction of platinum with mercury;[72-74] on strong heating it can be decomposed into $PtHg_2$ and PtHg.[72] The attack of mercury on platinum is affected by the presence of other metals. Aluminum, copper, indium, tin, and zinc inhibit the amalgamation of platinum, probably by forming intermetallic compounds with platinum on the surface. The formation of such compounds after the deposition of tin or zinc onto platinum electrodes has been reported.[75] Other metals, such as gold, lead, and silver have no effect on the interaction of platinum and mercury.[72]

The platinum-mercury system is important from the electroanalytical point of view because thin-film mercury electrodes, prepared by deposition of mercury onto platinum surfaces, are widespread in analytical use. Earlier electrochemical studies have shown that platinum-mercury compounds are formed when mercury is deposited onto the surface of a platinum electrode.[73,74,76-79] When the platinum surface is covered by these compounds (mainly $PtHg_4$), further electroreduction leads to the deposition of bulk mercury.

Oxidations of such electrodes have been carried out by a number of workers.[73,74,76-78] Constant-current oxidation shows three steps on potential-time or -charge curves. A typical potential-charge curve is shown in Figure 13. The first step, at +0.70 V, corresponds to the oxidation of the bulk mercury from the surface of the electrode. During the second step, mercury is oxidized from an intermetallic platinum-mercury compound, and the most positive step, at +1.85 V, corresponds to the evolution of oxygen.

Robbins and Enke[74] attempted to evaluate the free energy of formation of $PtHg_4$ by measuring the potential difference of the cell

$$Hg/Hg_2Cl_2, 0.1\,M, KCl, Hg_2Cl_2/PtHg_4.$$

Care was taken to obtain reproducible and reliable results, and the e.m.f. of the cell was found to be 87 mV. This value corresponds to a value of −8.0 kcal mol^{-1} for the standard free energy of formation of $PtHg_4$

$$Pt + 4Hg \rightarrow PtHg_4$$

at 25°C. However, this value is considerably lower than that found by Jangg and Steppan[57] by a non-electrochemical method. It is not easy to assign a reason for the discrepancy, but it seems to be possible that true equilibrium was not reached in the measurements made by Robbins and Enke.[74] The work of Kryska[67] on the palladium-mercury system has shown that the accuracy of potentiometric measurements was rather low because of the slowness of the chemical equilibria involved, and the same thing may be true in the platinum-mercury system.

Bruckenstein and co-workers[80] have recently studied the interactions of platinum and mercury using platinum ring-disc electrodes. On the basis of numerous and well-designed experiments, these authors arrived at the following conclusions. When the amount of deposited mercury is less than the quantity necessary to cover the platinum surface, assuming a stoichiometry of one atom of mercury per atom of platinum atom, there appears to be a compound having the formula Pt_2Hg, which has been identified in early works.[69,70] When a second monolayer is completely deposited, a surface state corresponding to $PtHg_2$ exists. On

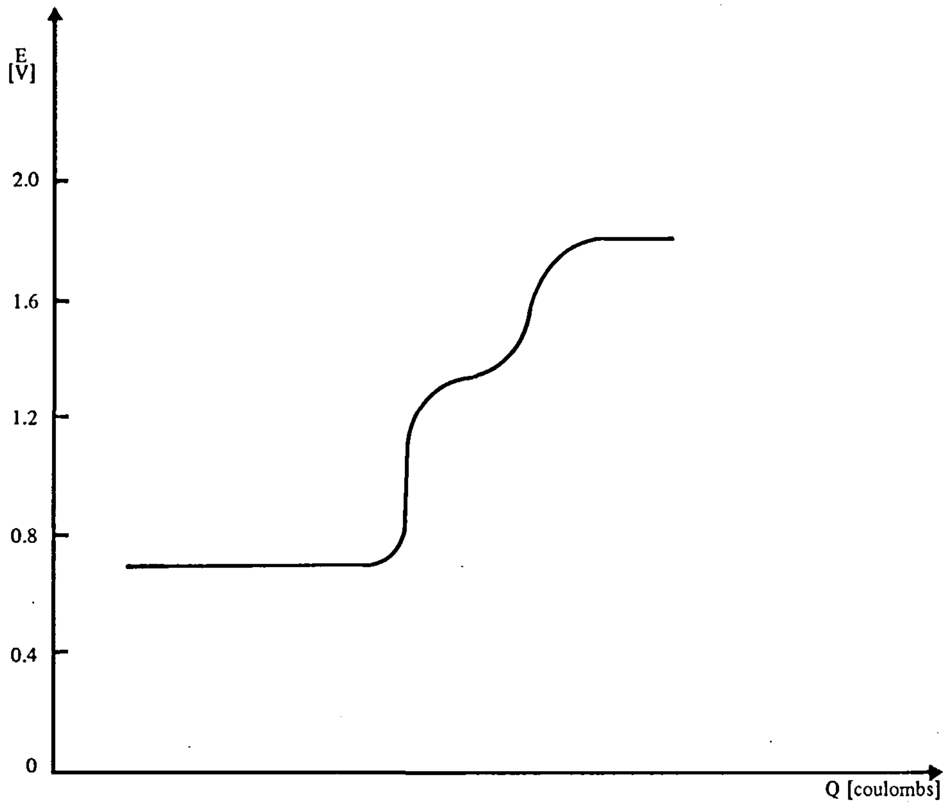

FIGURE 13. Variation of potential with charge for the stripping of a mercury-coated platinum electrode. Potentials are referred to the N.H.E.

oxidation, $PtHg_2$ is converted to Hg(II) and a monolayer of mercury on platinum (PtHg).

At least one other platinum-mercury species forms and penetrates beneath the platinum-solution interface as the next few monolayers of mercury are deposited. Bulk mercury exists in amounts comparable to the amount of subsurface Hg only after about 50 monolayers of mercury have been deposited on platinum. This bulk mercury is converted to the subsurface compound at a finite rate.

A relatively thick layer of mercury must be deposited onto a platinum electrode in order to achieve a uniform coating of the surface with liquid mercury, because the various surface and subsurface platinum-mercury compounds form readily. These compounds do not prevent further reaction of surface mercury with the bulk platinum. However, a fairly thick layer of the subsurface compounds can slow this reaction down, as has been shown by Hartley and other workers,[73,77,78] and thus provide a mercury-coated platinum electrode with a useable lifetime.

However, the prospects of preparing a mercury-covered platinum electrode that would be stable for long periods of time are poor, and electrode materials other than platinum should be considered if stable, thin mercury-film electrodes are to be prepared. It seems that still further work on the platinum-mercury system would be desirable. The electrodeposition of various platinum-mercury compounds onto inert (e.g., carbon) electrodes with further electrochemical investigations (stripping, potential measurements) would be fruitful. This short review of the electrochemical investigations that have been made of systems containing mercury and nickel-group metals shows their complexity. These systems are important from the analytical point of view, because mercury-film electrodes may be prepared by the deposition of mercury onto such metals. It seems that intermetallic compounds, especially those of the type $MeHg_4$, might be used as electrode materials. The overpotential for hydrogen evolution on these compounds is almost as large as for stationary pure mercury electrodes.

1.5.2. Manganese Amalgam

Heterogeneous manganese amalgam contains the intermetallic compounds MnHg and Mn_2Hg_5,[31] and the existence of Mn_3Hg_4 has also been suggested.[57] Mn_2Hg_5 is not very stable and decomposes on heating, even at 75°C, into MnHg and mercury.

The solubility of manganese in mercury is not large, and determinations by various methods yield values between 1 and 4 $\times$ 10^{-3} wt %. Electrochemical methods have been widely used in these determinations.[28]

The oxidation of manganese amalgams was investigated by Kemula and Galus.[27] With heterogeneous amalgams they observed three oxidation steps. These results were later questioned by Krasnova and Zebreva,[82] who claimed that only one anodic peak is observed during such oxidations.

However, Lange and Bukhman,[30] investigating the oxidation of manganese amalgams of various concentrations, found that at some limiting concentration exceeding the solubility of manganese in mercury, a new oxidation wave appears and that its height increases on further increasing the concentration of manganese. They described the nature of this second wave in subsequent papers.[29,84]

This wave is shown in Figure 14, which represents the oxidation of an amalgam some time after its preparation. The second step is easily visible at positive potentials. It is explained as reflecting the oxidation of the intermetallic compound Mn_2Hg_5, which proceeds by the dissolution of that compound before the charge-transfer step. Evidence for this conclusion is obtained from chronoamperometric current-time curves recorded at -0.40 V (vs. N.H.E.), on which, after an initial drop, the current was practically constant for a long time. Then, after the oxidation of intermetallic compound was practically complete, the current dropped almost to zero in a very short time.

Lange and Bukhman[84] calculated the rate constants for the oxidation of the intermetallic compound at different temperatures, and from these results computed the energy of activation.

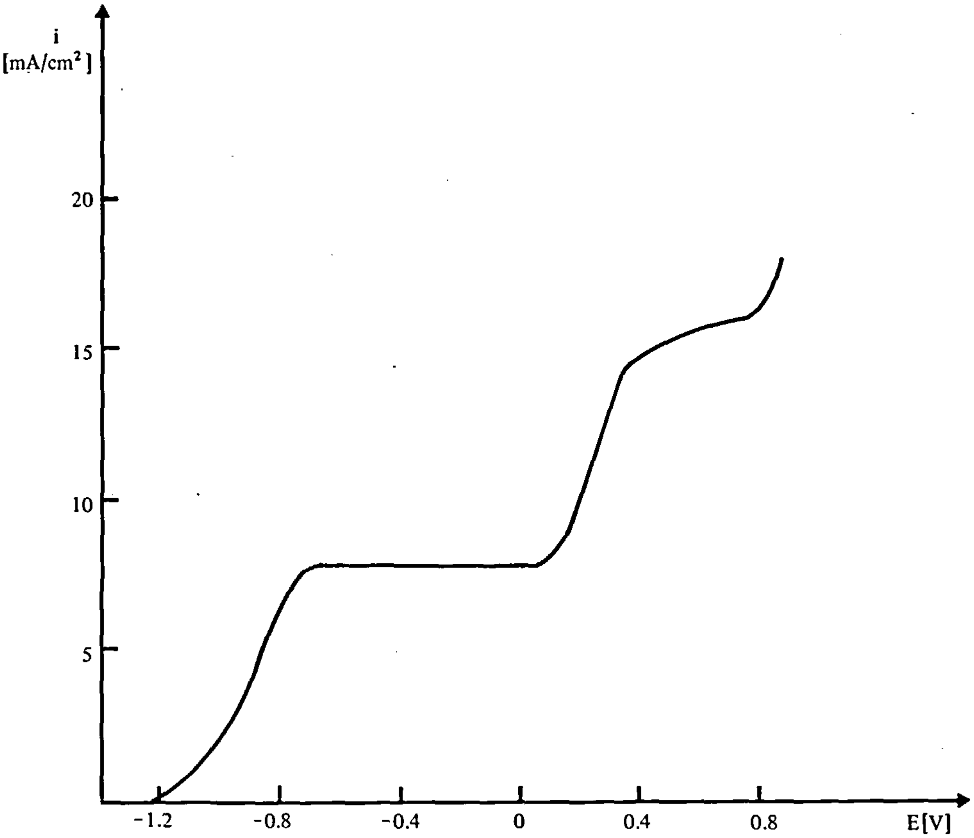

FIGURE 14. The dependence on potential of the current for the anodic oxidation of a manganese amalgam containing 0.0275% of manganese by weight. Potentials are referred to the N.H.E.

The resulting value, 9.65 kcal mol,$^{-1}$ also indicates the occurrence of a chemical step in the overall anodic reaction.

It was found that the amalgam is to some extent supersaturated when freshly prepared by electrodeposition, and that its state is closer to equilibrium for more concentrated amalgams. As may be expected, the rate of attainment of equilibrium is higher at elevated temperature and is increased by mixing of the amalgam.

It seems that further work on manganese amalgams is needed. The mechanism of oxidation of the intermetallic compound Mn_2Hg_5 especially should be investigated.

1.5.3. Cobalt and Iron Amalgams

These metals do not form intermetallic compounds with mercury, and their solubilities in mercury are very low. However, even quite concentrated heterogeneous amalgams of these metals can be prepared by the electroreduction of cobalt (II) or iron(II) at mercury electrodes under the proper conditions.[54,85] Such amalgams have been shown to consist of finely divided metal crystallites suspended in mercury,[54,85] and are quite stable.[86] Under normal conditions, these metals are not wetted by mercury.

The iron-mercury system has not been studied intensively by electrochemical techniques; cobalt amalgams have received more attention. In these investigations, the electroreduction of cobalt(II) at mercury electrodes was usually studied as well as the electrooxidation of the amalgams. Cobalt amalgam may also be easily prepared by the electroreduction of cobalt(II) at mercury microelectrodes such as the HMDE. The oxidation of cobalt deposited on the hanging mercury-drop electrode is quite complicated since several oxidation steps are often observed.[58,87] The existence of diatomic cobalt has been suggested on the basis of electrochemical investigations,[87,88] but has not been confirmed in more recent investigations.

It has been found that cobalt, when electrochemically generated at mercury electrodes, does not always enter into the mercury phase. Very often when the reduction proceeds in the presence of thiocyanate or another ligand containing sulfur, the cobalt remains on the surface of the mercury electrode.[48]

This is probably due to the formation, during the course of the electrode process, of CoS which is adsorbed onto the electrode surface. This adsorbed layer hinders the wetting and amalgamation of cobalt and also its amalgam formation. It seems that the results of Astley and Harrison[89] may also be interpreted from this point of view.

In general, it may be assumed that microcrystals of cobalt are formed in the first step of the electroreduction of cobalt(II) from various background electrolytes. The entrance of cobalt into the mercury phase depends on increases of the interfacial tensions at the boundaries between the microcrystals and the solution and between the mercury and the solution.[90] This may be connected with some difference of potential between mercury and microcrystals, since the electroreductions of cobalt(II) and hydrogen ions on cobalt microcrystals proceed more readily than they do on mercury. A significant role in the wetting of microcrystals is probably played by the partial oxidation of their surfaces, which is increased by decreasing either the negative potential of the investigated electrode or the acidity of the solution.

On the basis of published experiments, one may conclude that the electrochemical behavior of the iron-mercury system should be similar.

Some information about the electrochemical behaviors of iron and cobalt amalgams may be obtained from investigations of the electrode kinetics of amalgam electrodes. The exchange currents of cobalt-amalgam electrodes have been determined[81] in solutions of chlorides and sulfates. Cobalt amalgam has been anodically oxidized by Jangg.[83]

Eriksrud and Hurlen,[91] investigating the kinetics of the Co(II)/Co(Hg) electrode in chloride solutions, found that there seems to be little doubt that charge-transfer in this system is effected mainly by cobaltous ions directly between the hydrated and amalgamated states. Anodic investigations of concentrated heterogeneous cobalt amalgams showed no sign of sluggishness in either transport or in chemical reactions of cobalt species. This may indicate that the transport to the interphase is partly by cobalt crystallites, which exchange atoms rapidly with the homogeneous phase to keep it saturated.

In the Fe(II)/Fe(Hg) system, the cathodic charge was also found[92] to be transferred directly to the liquid amalgam, and there was no indication that the cathodic charge-transfer occurs at crystallites, which are probably present to some extent on the amalgam surface. In iron-rich amalgams the anodic process is governed mainly by hydrogen oxidation,[92] while the oxidations of concentrated amalgams of cobalt and nickel were found to be controlled by metal dissolution.[91,93] Further work should be carried out along these lines.

The potentials of iron and cobalt amalgam electrodes have been also measured.

Hurlen and Breiland[92] have investigated the potentials of iron amalgams, and found that they increase, and approach the original potential of pure mercury in the same solution, when the cathodic current is interrupted. Zarechanskaya et al.[94] have found that the potentials of iron and iron-amalgam electrodes in sulfuric acid solutions are identical at temperatures exceeding 100°C, and are close to those calculated from thermodynamic data. Similar observations were reported[94] for cobalt and cobalt-amalgam electrodes, but for temperatures exceeding 160°C.

The dependence of measured potentials on temperature is shown in Figure 15. The results presented may, in turn, be interpreted as indicating the direct participation of the solid metal phase in the potential-determining process.

1.5.4. Copper Amalgam

Copper reacts with mercury to form the intermetallic compound Cu_4Hg_3, which decomposes at temperatures exceeding 96°C. However, Jangg and Kirchmayr found[3] that the potential of the saturated amalgam is equal to that of a pure copper electrode. This points to a very low energy of formation of the copper-mercury compound (see Section 2.1). It should be said, however, that Schupp et al.[149] have found a difference of 5 mV between the potentials of these electrodes.

Potentiometric investigations[3] have shown that the potential of copper amalgam electrodes obey the Nernst equation over the range of concentrations from 10^{-5} to 10^{-2} *M*. On the basis of these data, Jangg and Kirchmayr conclude that there is no interaction between copper and mercury in liquid copper amalgams.

Levitskaya and Zebreva[150] have also studied

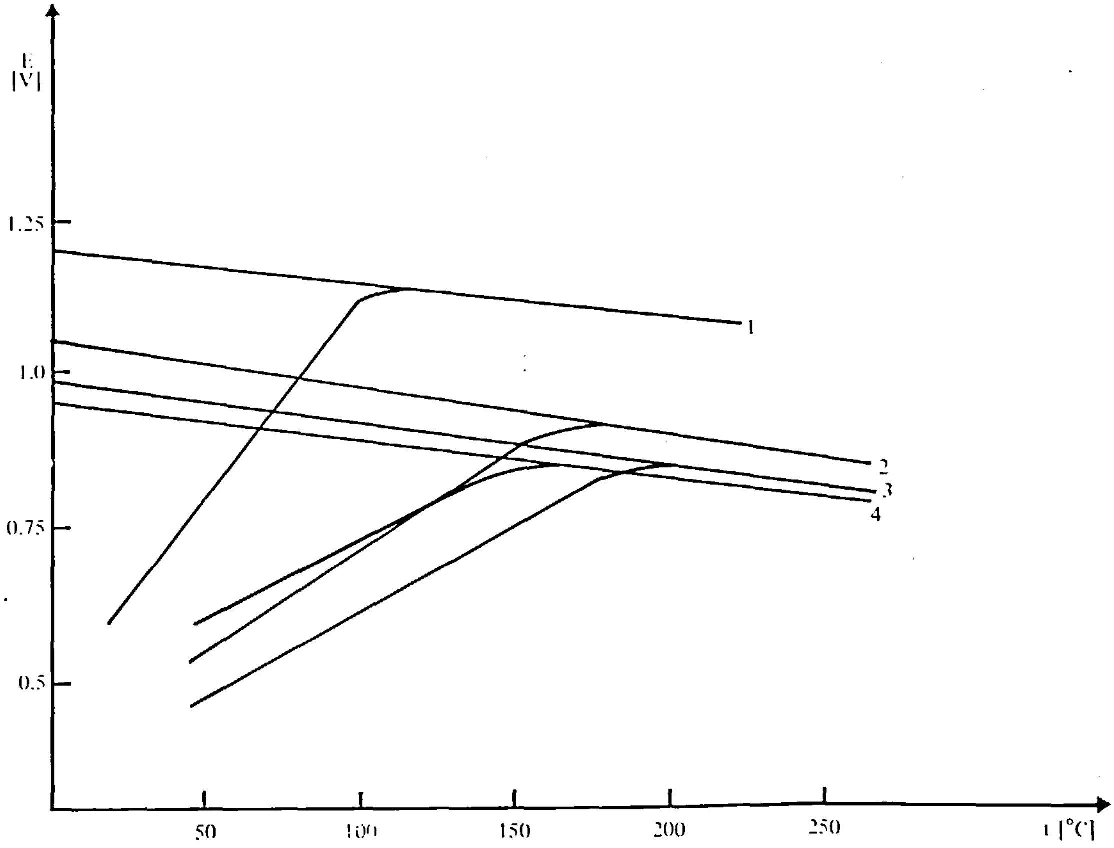

FIGURE 15. Dependence on temperature of the stationary potentials of (1) iron, (2) cobalt, and (3) nickel in sulfate solutions. Curve 4 shows the dependence for nickel amalgam in hydrochloric acid. The concentration of the potential-determining ion is 0.5 *M* for each curve.

the potentials of copper amalgam electrodes, and have done so at higher temperatures (40, 50, and 80°C) as well as at room temperature. At 40 and 50°C, the potentials of copper amalgam electrodes obeyed the Nernst equation, but at 80°C, reproducible results could not be obtained because of interaction of copper with the electrolyte.

Different results were obtained by Chao and Costa[151] in their study of the copper amalgam. In careful experiments they found a difference of 6 mV between the potentials of copper and copper amalgam electrodes in the same solution. In heterogeneous amalgams, the solid phase that is in equilibrium with the saturated amalgam is CuHg. The formation of this compound is slow. There is also some evidence for the existence in saturated amalgams of a copper-mercury compound that is soluble in the mercury phase.

1.5.5. Amalgams of Other Transition Metals

Electrochemical investigations of other transition-metal amalgams are not sufficiently developed. This is probably because the solubilities of these metals in mercury are generally very small and because the potentials at which they undergo dissolution into aqueous solutions are quite negative.

Recent work in this area has included an investigation of the electrodeposition of chromium at mercury electrodes.[95] Chromium does not form intermetallic compounds with mercury, and its amalgam has properties similar to those of iron amalgam.[96] Similarly, molybdenum and tungsten practically do not react with mercury. Their solubilities in mercury are of the order of 10^{-5} wt %.

Amalgams of the titanium-group metals are more interesting from the chemical point of view. It has been found that titanium forms several compounds with mercury,[97] and that zirconium also interacts with mercury.[97] The solubilities of the titanium-group metals in mercury are also very low.

Electrochemical investigations of amalgams of these and other transition metals should be carried more intensively in the future with due attention to the choice of conditions. Non-aqueous solvents will prove to be especially useful in such studies of metals that have very negative redox potentials.

1.5.6. Antimony Amalgam

Antimony does not form intermetallic compounds with mercury and its solubility in mercury is low, equal to 5×10^{-4} atom percent at room temperature.

The oxidation of antimony amalgams has been studied repeatedly with both micro- and macro-electrodes. Bukhman and Dragavtseva[98] showed that the oxidation current of an antimony amalgam continues to increase with increasing antimony concentration, even in the range of concentrations that exceeds the solubility of antimony in mercury. They explained this behavior by assuming that the dispersed solid antimony participates in the anodic process.

Zakhartshuk and Zebreva,[99] using hanging mercury-drop electrodes, arrived at different conclusions. According to them, the anodic process involves the participation of metallic antimony that has been deposited onto the surface of the mercury in the cathodic step. However, Lange and Bukhman[100] do not consider such a mechanism to be very probable with diluted amalgams. They studied the anodic oxidation of antimony amalgams over the range of temperatures from 20 to 80°C, and calculated the solubilities of antimony at various temperatures from the limiting currents, with the results given in Table 6.

A plot of the anodic limiting current of antimony against its concentration in the amalgam shows two breaks (Figure 16). The second segment of this plot may reflect, according to the authors, the participation of some other form of antimony, in addition to the atomic form, in the anodic process.

The authors calculated that the heat of dissolution of antimony in mercury is 5.5 kcal mol,$^{-1}$ which agrees well with the value of 5.4 kcal mol^{-1} found by Jangg and Pallman[62] over the range of temperatures from 100 to 150°C. This agreement suggests that dissolution of antimony occurs by the same mechanism over the whole range of

TABLE 6

Solubility of Antimony in Mercury at Different Temperatures

Temperature (°C)	Solubility (atom percent)
20	0.9×10^{-3}
40	1.75×10^{-3}
60	2.55×10^{-3}
80	3.4×10^{-3}

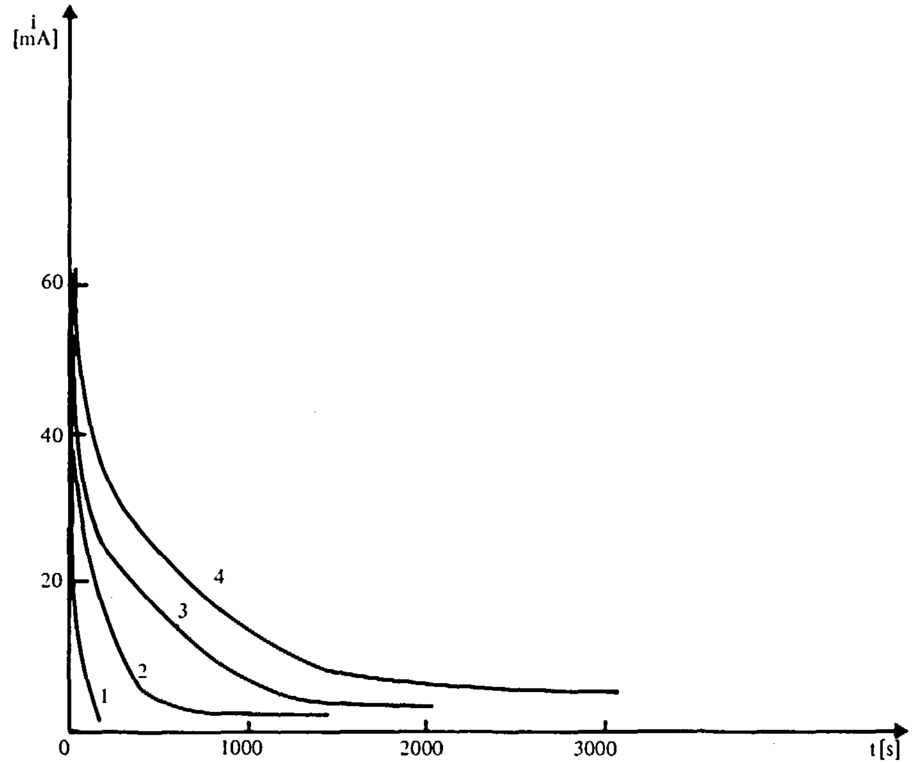

FIGURE 16. Current-time curves for the anodic oxidation of antimony amalgams at 40°C. The concentrations of antimony in the amalgam were (1) 1.72×10^{-3}, (2) 1.10×10^{-2}, (3) 1.9×10^{-2}, and (4) 3.8×10^{-2} atom percent.

temperatures from 20 to 150°C. The activation energy for the oxidation of a homogenous amalgam is equal to 1.32 kcal mol^{-1} showing that this process is limited by the rate of transport of antimony atoms to the interface.

The rate constants for the oxidation of heterogeneous antimony amalgams are considerably lower than those found for homogeneous ones, which also suggests that particles larger than monatomic ones participate in the oxidation process.

1.5.7. Indium Amalgam

Indium is one of the metals that are most highly soluble in mercury: a saturated solution in mercury contains 55% of indium by weight. Physicochemical investigations[101] have shown the following intermetallic compounds to be present in the indium-mercury system: $InHg_6$, $InHg_4$, $InHg_3$, In_5Hg_9, InHg, In_7Hg, and $In_{11}Hg$.

It has been found that the interactions of these metals at temperatures exceeding the liquidus temperature are characterized by significant negative deviations from the behavior of ideal solutions as a result of formation of the ordered structure of the intermetallic compound in the liquid homogeneous amalgam.

Kozin and Dergatsheva[102] studied the natures and compositions of the intermetallic compounds that exist in liquid indium amalgams. The stabilities of these compounds are widely different. The compound $InHg_6$ exists only in the solid state[102] and decomposes at room temperature. Investigations of the electrical conductivities of indium amalgams show that the stable compounds are $InHg_3$ and InHg.

To determine the composition of the compound that is formed, Kozin and Dergacheva[102] used earlier published potentiometric results.[103, 104]

In Figure 17, the recalculated results are given in terms of the e.m.f. of the cell

$$\text{In/electrolyte containing } In^{3+}/\underset{N_1 = x}{In_x\,(Hg)}$$

and the mole fraction N_1 of indium in the

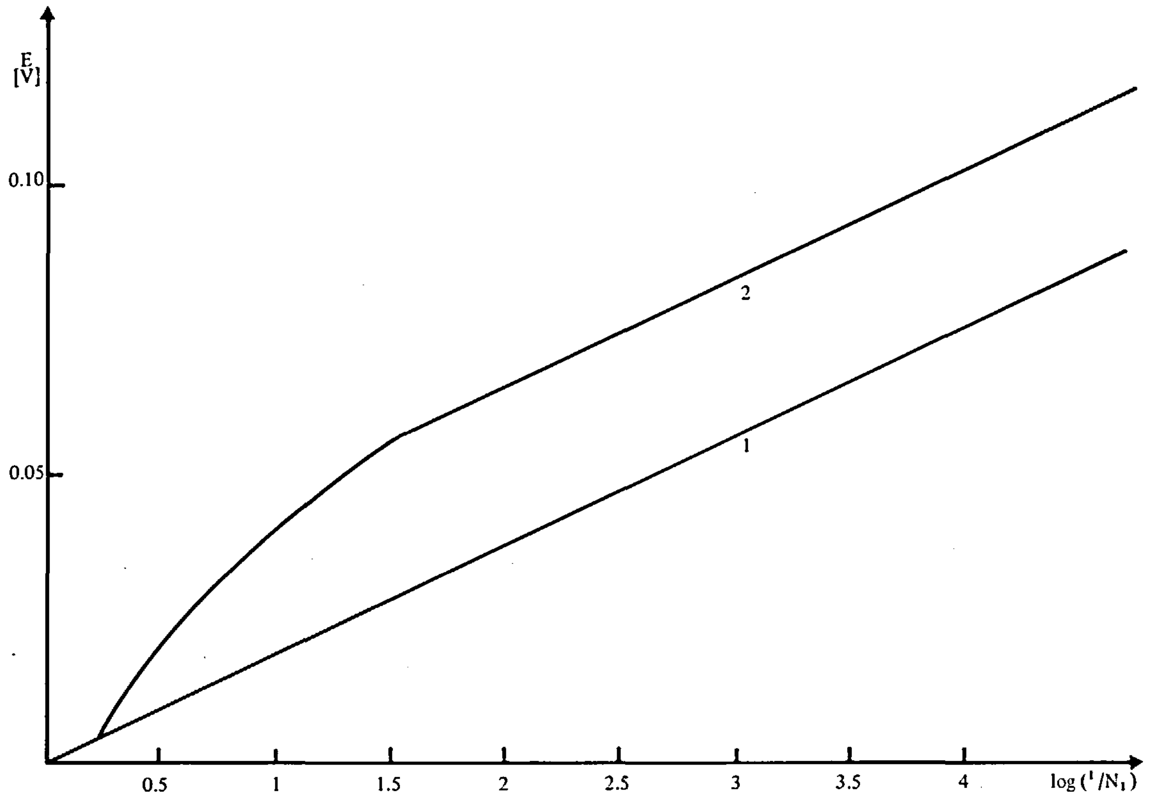

FIGURE 17. Dependence of e.m.f. of the concentration cell on log $1/N_1$ (N_1 = mole fraction of indium). Curve 1 was calculated on basis of Equation 1.5; curve 2 is the experimental curve.

amalgam. Curve 1 shows the theoretical dependence according to the Nernst-Turin equation

$$E = \frac{RT}{nF} \ln \frac{1}{N_1} \qquad (1.5)$$

The shape of the experimental curve points to the formation of an intermetallic compound that weakly dissociated in the mercury. Further analysis of the experimental data shows that the composition of this compound may be represented by the formula $InHg_3$. Its dissociation constant is equal to 5.3×10^{-2} at 25°C.

1.5.8. Germanium Amalgam

There is no agreement in the chemical literature on the solubility of germanium in mercury. According to Kozin,[105] its solubility, calculated on the basis of an empirical formula, is only of the order 10^{-18} atom percent. It should be said that this result is very approximate. In addition, Kozin writes[105] that germanium amalgam cannot be prepared by the electroreduction of germanium ions at mercury electrodes.

On the other hand, this metal has been determined[106,107] by the anodic stripping method after prior accumulation at hanging mercury-drop electrodes. This would be rather difficult if the solubility were as low as is reported by Kozin: one would then expect the reproducibility of the results to be rather poor. Moreover, Bock and Mackstein[108] produced a relatively concentrated amalgam, containing 0.017 wt % of germanium by electrolysis.

The solubility of germanium in mercury has been investigated experimentally by an electrochemical method using the HMDE.[109] This method was briefly discussed in Section 1.2. It was found that the dependence of the peak height for the anodic oxidation of germanium initially deposited at the HMDE on the concentration of germanium in the amalgam was linear up to 1.8×10^{-4} *M*, with a precision of 10 to 15%. On increasing the concentration further, the peak height decreased slightly. Since the anodic peaks had rather normal shapes, the authors assumed that the oxidation proceeds from the homogeneous amalgam, and considered the value $1.8 \times$

10^{-4} *M* to be the solubility of germanium in mercury at 25°C.

The decrease of the anodic current at antimony concentrations higher than 1.8×10^{-4} *M* was accounted for by an increase of the amalgam viscosity and a decrease of the working part of the electrode. However, this phenomenon may also be explained in another way by assuming that a supersaturated amalgam is formed during electroreduction. At higher concentration, this amalgam crystallizes more rapidly in approaching the equilibrium state. A similar dependence has been observed by Kemula and Galus for nickel amalgam, where the formation of supersaturated amalgam is a well-recognized fact and is responsible for the appearance of a peak on a plot of the anodic peak current against the amalgam concentration. Such an explanation has been advanced recently by Kublik and Gruszka.[110,111] On the basis of experimental results, they arrived at the conclusion that the electrolysis of dilute solutions of germanium ions may lead to the formation of unstable supersaturated germanium amalgams which crystallize in time. The crystallization rate is higher for more concentrated amalgams.

One may according conclude that the solubility of germanium in mercury given by Stepanova and Zakharov[109] is incorrect, and that their value gives the concentration of the supersaturated amalgam at some stage of supersaturation.

The solubility given by Kublik and Gruszka is equal to 3×10^{-6} *M*.

1.5.9. Zinc, Tin, and Cadmium Amalgams

There are also several intermetallic phases in the zinc-mercury system. The solubility of zinc in mercury is large; it is equal to 5.83 atom percent at 20°C. Liquid zinc amalgams have been used by many workers in electrochemical investigations of charge transfer in the $Zn^{2+}/Zn(Hg)$ system, and have been produced by numerous workers by the electroreduction of zinc ions at mercury electrodes. Though this amalgam is widely used, the form of existence of zinc atoms in the mercury phase is not well known.

Ficker and Meites,[88] investigating the reaction between zinc and cobalt in mercury by stirred-pool chronopotentiometry, arrived at the conclusion that it occurs between diatomic zinc and cobalt species, and this was subsequently concurred with by Hovsepian and Shain.[89] Similar observations on the behaviors of mixed amalgams of copper and zinc showed[113] that the aggregation numbers of copper and zinc are equal in amalgams, so that if zinc is diatomic, copper is also diatomic. However, measurements of the potentials of copper amalgams in contact with solutions containing copper(II) showed that the half-reaction is $Cu(II) + 2e \overset{Hg}{\rightleftharpoons} Cu(Hg)$, rather than $2Cu(II) + 4e \overset{Hg}{\rightleftharpoons} Cu_2(Hg)$.

Rodgers and Meites[114] have recently studied the oxidation of zinc amalgam by double-potential-step chronoamperometry in an attempt to confirm the observations of Hovsepian and Shain, who had used this technique, and to find out whether diatomic molecules of zinc exist in zinc amalgam. The dropping electrode, having a drop time of 22.5 s, was maintained at −0.2 V for the first 17.5 s of its life and the potential was then stepped to −1.2 V, maintained at this potential for a time that was varied from 2 to 800 ms, and then again stepped to −0.2 V.

The agreement of the experimental parameters $\frac{i_r}{i_f}$ with that calculated from the equation

$$\frac{i_r}{i_f} = \left(\frac{t_f}{t_r}\right)^{1/2} \left[1 - \left(\frac{t_r/t_f}{1 + t_r/t_f}\right)^{1/2}\right] \qquad (1.6)$$

derived[115] for a diffusion-limited process contradicted the results of Hovsepian and Shain, provided no support for the existence of a dimeric form of zinc in its amalgams, and showed that if dimers do exist, their formation must be very slow.

In Equation 1.6, i_f is the cathodic current at the instant when the second potential step is applied, and i_r is the anodic current at an instant t_r.

Similar conclusions were obtained by Rodgers and Meites[114] from isopiestic measurements with zinc amalgams.

Further investigations of this type or a similar one with other amalgams are needed to reveal whether dimers or bigger conglomerates of metal atoms are formed by other metals in the mercury phase.

Elliott has potentiometrically investigated[112] tin amalgams containing from 0.001 to 0.128 mol fraction of tin at 520 to 570°K. He found that in the most dilute solutions the tin atoms randomly occupy any atomic positions. As the concentration is increased (above 0.01 mol fraction Sn at 525°K), tin loses 1/3 of its entropy of mixing, quite possibly by moving into sheets within which the positions of tin atoms are two-dimensionally random.

The enthalpy linearity seems to rule out simple association to form molecules of Sn_2 or Sn_3. Some interaction may also be expected to occur in cadmium amalgam.

Diatomic species have not been detected in cadmium amalgams. Kozin and Dergacheva[116] interpret the results of measurements of the e.m.f. of the cell

$$\mathrm{Cd/electrolyte\ Cd^{2+}/Cd_xHg} \qquad (1.7)$$

in terms of the formation of an intermetallic compound of cadmium and mercury that is soluble in the amalgam phase. The measurements were carried out in the range of temperatures from 25 to 250°C. The composition of the intermetallic compound was found to be $CdHg_3$. The authors claim that at low temperatures (25 to 75°C) this compound remains in equilibrium with a solid phase. Its dissociation constant, calculated from the data of Bijl,[117] is equal to 2.4 at 25°C, to 2.8 at 50°C, and to 3.3 at 75°C.

1.5.10. *Amalgams of the Alkali and Alkaline Earth Metals*

Amalgams of the alkali and alkaline earth metals are interesting because these metals undergo strong chemical interactions with mercury. These interactions are clearly evinced by electrochemical measurements. It is known that standard potentials of redox systems involving the alkali metals and their ions, Me^+/Me, are close to -3 V vs. N.H.E., while those of redox systems of the alkaline earth metals, Me^{2+}/Me, are slightly more positive.

All these metals show significantly less negative potentials for the redox systems $Me^+/Me(Hg)$ and $Me^{2+}/Me(Hg)$, where the reduced form is the amalgam of the appropriate metal. The potentials of these amalgam electrodes are easily determined; for the $Na^+/Na(Hg)$ and $K^+/K(Hg)$ systems, they are approximately equal to -1.9 V vs. N.H.E. These differences between equilibrium potentials exceed 1 V, and are due to a chemical reaction between mercury and the alkali or alkaline earth metal. This reaction may be observed to proceed violently when one adds such a metal to mercury.

Korshunov et al.[118] give rather reliable values of the potentials for the $Me^+/Me(Hg)$ electrodes in aqueous solutions at 25°C. In a more recent paper, Khlystova and Korshunov[119] report such values for the electrodes $Me^{2+}/Me(Hg)$ involving the alkaline earth metals. Stromberg and Konkova[120] evaluated the standard potential for ammonium amalgam, which is not very stable. They found the value to be -1.70 V vs. N.H.E.; this is close to the half-wave potential for the electroreduction of ammonium ion, indicating that this electroreduction is rather reversible.

Although there is no doubt that chemical interactions do occur between mercury and the dissolved metals in these amalgams, the compositions of the products of these interactions are still a matter of discussion. In solid amalgams, a number of intermetallic compounds have been detected. For instance, sodium amalgams have been found to contain the compounds $NaHg_4$, $NaHg_2$, Na_7Hg_8, NaHg, Na_3Hg_2, Na_5Hg_2, and Na_3Hg.

In dilute homogeneous amalgams, Kozin and Dergacheva[116] believe that there also exist intermetallic compounds having definite compositions. From previously published[121] values of the e.m.f.s of the cell

$$\mathrm{K/K^+ + melt/K_x(Hg)} \qquad (1.8)$$

at 275 and 325°C, they deduced the existence of the compound KHg_2, which is soluble in the mercury phase. This compound is the most stable one in the potassium-mercury system;[122] its dissociation constant is equal[116] to 7×10^{-8}.

The e.m.f.s of similar cells containing sodium electrodes[123,124] at 25°C are also interpreted by Kozin and Dergacheva in terms of the formation of soluble intermetallic compounds having definite compositions. Finally, they attach a similar interpretation to measurements of the potentials of alkaline earth metal electrodes. They evidently assume[116] that homogeneous magnesium amalgams contain the compound MgHg, which is the most stable one[125] in the magnesium-mercury system.

On the other hand, Ruban et al.[126] assume that homogeneous sodium and potassium amalgams do not contain compounds having definite compositions. They measured the e.m.f. of the following concentration cell

$$\mathrm{\underset{C}{Na/Hg}/Na^+/\underset{C_1}{Na(Hg)}} \qquad (1.9)$$

where the concentration C of sodium in the left-hand half-cell was kept constant. The results show that intermetallic compounds are formed in this system. To determine the amounts of mercury bonded to sodium in liquid amalgams at 25 and 50°C, these authors used the equation given by Hildebrand[127]

$$\Delta E = \frac{2.3RT}{nF} \left\{ m \log \frac{N_2 - m}{N_1 - m} - (m - 1) \log \frac{N_2 - m + 1}{N_1 - m + 1} \right\} \tag{1.10}$$

where m is the number of mercury atoms bonded to one sodium atom, N_1 is the ratio of the number of moles of mercury to the number of moles of sodium in the concentrated amalgam, and N_2 is the corresponding ratio for the dilute amalgam.

Although it was assumed, in the derivation of this equation, that m is constant over the range of compositions investigated, Ruban et al.[126] found that m depends on the amalgam concentration. On increasing the concentration of sodium in the amalgam from 0.65 to 7.19 *M* at 25°C, m decreases from 16 to 5–6. The higher of these concentrations corresponds to an almost saturated amalgam. Similar results were found for 50°C. The same authors performed similar measurements for concentration cells involving potassium amalgams, and obtained m = 15–16 for nearly saturated amalgams at 25°C. Here again m was found to depend on the amalgam concentration. On the basis of these results, the authors concluded that sodium and potassium amalgams do not contain molecules of intermetallic compounds having definite compositions. One should rather speak about the solvation of atoms of alkali metals by atoms of mercury. On this basis, one may distinguish between a first solvation shell and further ones.

These groups of workers[116,126] analyzed their experimental results in different manners in addition to using different cells, and these differences might have led them to quite different conclusions. Nevertheless, the concepts of both Kozin and Dergacheva[116] and Ruban et al.[126] may be close to the truth, since a molecule of intermetallic compounds having a definite formula may be further solvated by mercury atoms.

As follows from the foregoing discussion, the compositions of the intermetallic compounds that exist in homogeneous amalgams containing the alkali and alkaline earth metals are open to discussion and need further attention. The natures of the forces existing in such molecules should also be studied in the future.

1.6. Corrosion of Amalgams

It is well known that an amalgam of a metal having a negative redox potential may easily be oxidized by oxygen or by another oxidant present in the solution in contact with the amalgam. The ions of metals having more positive potentials may act as oxidants. The following reaction may then occur:

$${}_1Me^{n+} + {}_2Me(Hg) \leftrightharpoons {}_2Me^{n+} + {}_1Me(Hg) \tag{1.11}$$

assuming that the metals ${}_1Me$ and ${}_2Me$ form stable ions of the same valency.

The literature describes numerous studies of the kinetics and mechanisms of decomposition of amalgams under the action of various oxidants. The slowest step of such an oxidation is usually the diffusion either of ions in the solution or that of metal atoms in the amalgam phase.[128,129,133] Such chemical oxidations of metals from their amalgams are of importance in electroanalytical chemistry. Metal-ion impurities in the solution are very often determined by reduction and preconcentration in hanging mercury-drop electrodes followed by electrooxidation. Any reaction between the amalgam and an oxidant present in the solutions would complicate the determination.

Such reactions seem to be at least partly responsible for the deviations of the potentials of amalgam electrodes from the behavior predicted by the Nernst equation.

The problem of the chemical attack of oxygen on amalgams has been studied recently in several papers.[130–133] Chao and Costa[130] studied the corrosion of copper amalgam, and quantitatively assessed the influence of the amalgam concentration, of the partial pressure of oxygen, and of the pH.

Pelletier et al.[132] made a potentiometric study of the oxidation of dilute lead amalgam by oxygen dissolved in water. The purpose of this study was to find a method for the quantitative determination of traces of oxygen in gases. In a subsequent paper, these workers[133] described theoretically the time dependence of the potential of an amalgam electrode undergoing attack by oxygen. The amalgam electrode was assumed to have the shape of the drop, and the chemical reaction was considered to be much faster than mass-transport of either of the reacting species.

The following equation was obtained: ·

$$E = E_0 + \frac{RT}{nF} \ln \frac{mC_{O_2}\ D_{O_2}}{D_{Ox}} - \frac{RT}{nF} \ln \left\{ C_R^0 \frac{3mC_{O_2}\ D_{O_2}\ t}{\delta r_0} - \frac{mC_{O_2} r_0 D_{O_2}}{5\delta D_R} \right\} \quad (1.12)$$

It is valid only for times exceeding 30 s; a more complicated equation that is also valid for shorter times may be found in the original paper.[133] In Equation 1.12, m is the number of oxygen molecules consumed in reacting with one metal atom of the amalgam; r_0 is the radius of the electrode; δ is the thickness of the diffusion layer; C_{O_2} and D_{O_2} are the diffusion coefficient and the concentration of oxygen in the bulk of the solution; C_R^0 and D_R are the initial concentration and the diffusion coefficient of the metal in the amalgam; and D_{Ox} is the diffusion coefficient of the metal ions in the solution; the other symbols have their usual significances.

Experimental results for the oxidations of zinc, cadmium, and lead amalgams are in good agreement with this theoretical equation. This shows that diffusion of the reacting species is the slowest step in such oxidation reactions.

Interfering chemical oxidation in the chronopotentiometric oxidation of amalgams was studied by Barański and Galus.[134] Two cases were considered theoretically: (i) the oxidation of metal from a semi-infinite field, and (ii) the oxidation of amalgam from the HMDE. The protection of amalgam against interfering chemical oxidation during chronopotentiometric oxidation has also been considered. Satisfactory agreement of theoretical with experimental results was found for the oxidation of zinc amalgam by cadmium ions, which again points to diffusion as the slowest step in the overall reaction.

2. POTENTIALS OF AMALGAM ELECTRODES

Amalgam electrodes have been used for a long time in electrochemical studies, and continue to play an important role today (see, for instance, Reference 135). This section deals with the potentials of such electrodes and begins consideration of the potentials of heterogeneous amalgams.

2.1. Potentials of Heterogeneous Simple Amalgams

The relation between the potentials of a metal electrode and of an amalgam electrode constructed from the same metal, both dipped in the same solution, is important, both theoretically and practically, in electroanalytical chemistry.

Early studies of this problem have been carried out by Stackelberg[136] and Lingane,[137] who considered the relation among the normal potential of the metal electrode, the polarographic half-wave potential, and the solubility of the metal in mercury for reversible electrode reactions. On the basis of simple relations,[138] it was possible to obtain a satisfactory explanation of the differences between the standard potentials of the metals and the half-wave potentials for a number of redox systems. As is widely known, this difference is largest for the alkali and alkaline earth metals because of the interactions of these metals with mercury, which result in the formation of intermetallic compounds and alter the potential by approximately 1 V.

The relation between metal- and amalgam-electrode potentials was later considered by Jangg and Kirchmayr[3] on a thermodynamic basis, and their treatment is briefly summarized here with changes introduced later by Zebreva et al.[140] One should add that the relation between the potential of an amalgam electrode and the concentration and structure of the amalgam was theoretically considered by Chao and Costa.

For a heterogeneous amalgam in which the solid phase is composed of pure metal, the chemical potentials are equal for both phases of the saturated amalgam, and the potential of the metal electrode should be exactly equal to the potential of the saturated amalgam electrode.

Let us assume now that the metal introduced into mercury forms an intermetallic compound with mercury, and that the liquid phase in the saturated amalgam is in equilibrium with crystals of the intermetallic compound as the second phase. Thus, the amalgam under consideration is saturated.

This formation of the compound may be represented by the equation

$$\mathrm{Me} + x\,\mathrm{Hg} \rightleftharpoons \mathrm{MeHg_x}\ (\mathrm{solid}) \quad (2.1)$$

and equilibrium between the solid and liquid phases may be described by writing

$$\mu_{\mathrm{Me(sat)}} + x\mu_{\mathrm{Hg(sat)}} = \mu^0_{\mathrm{MeHg_x(solid)}} \quad (2.2)$$

where $\overset{o}{\mu}_{\text{MeHg}_x\text{(solid)}}$ is the standard chemical potential of the intermetallic compound, and $\mu_{\text{Me(sat)}}$ and $\mu_{\text{Hg(sat)}}$ are the chemical potentials of the metal and mercury, respectively, in the saturated amalgam.

If the intermetallic compound is formed according to Equation 2.1 from the pure elements, the standard free-energy change ΔG^o for that reaction is

$$\Delta G^o = \mu^o_{\text{MeHg}_x\text{(solid)}} - \mu^o_{\text{Me}} - x\mu^o_{\text{Hg}} \qquad (2.3)$$

where $\mu^o{}_{\text{Me}}$ and $\mu^o{}_{\text{Hg}}$ are the standard chemical potentials of the pure metal and mercury, respectively.

From Equations 2.2 and 2.3, one obtains

$$\Delta G^o + \mu^o_{\text{Me}} + x\mu^o_{\text{Hg}} = \mu_{\text{Me(sat)}} + x\mu_{\text{Hg(sat)}} \qquad (2.4)$$

Since $\mu_{\text{Hg(sat)}}$is described by the simple equation

$$\mu_{\text{Hg(sat)}} = \mu^o_{\text{Hg}} + RT \ln e_{\text{Hg(sat)}} \qquad (2.5)$$

Equation 2.4 yields

$$\Delta G^o + \mu^o_{\text{Me}} = \mu_{\text{Me(sat)}} + x\,RT \ln a_{\text{Hg(sat)}} \qquad (2.6)$$

Introducing $\mu_{\text{Me}}{}^{n+}$, the chemical potential of the metal ions in the solution on each side of Equation 2.6, one obtains

$$\Delta G^o + \mu^o_{\text{Me}} - \mu_{\text{Me}^{n+}} = \mu_{\text{Me(sat)}} - \mu_{\text{Me}^{n+}} + x\,RT \ln a_{\text{Hg/(sat)}} \qquad (2.7)$$

The potential of the amalgam is determined by the half-reaction

$$\text{Me}^{n+} + ne + \text{Hg} \rightleftharpoons \text{Me(Hg)} \qquad (2.8)$$

and is related to the difference between the chemical potentials of the metal in amalgam and the metal ions in the solution

$$E = \frac{\mu_{\text{Me}^{n+}} - \mu_{\text{Me(amalgam)}}}{nF} \qquad (2.9)$$

If one applies Equation 2.9 to the saturated amalgam, one obtains from Equation 2.7

$$E_{\text{Me(sat)}} - E_{\text{Me}} = -\frac{\Delta G^o}{nF} + \frac{x\,RT}{nF} \ln a_{\text{Hg(sat)}} \qquad (2.10)$$

where $E_{\text{Me(sat)}}$ and E_{Me} represent the potentials of the saturated amalgam and the metal electrode, respectively, in solutions containing the metal ions Me^{n+} at the same activity.

This equation may be rewritten in the form

$$E_{\text{Me(sat)}} = E^o_{\text{Me}} - \frac{\Delta G^o}{nF} + \frac{xRT}{nF} \ln a_{\text{Hg}} + \frac{RT}{nF} \ln a_{\text{Me}^{n+}} \qquad (2.11)$$

It follows from Equation 2.11 that a difference between the potentials of the amalgam and metal electrodes will be observed if Reaction 2.1 proceeds. The larger the change of free energy involved in that reaction the larger is the difference between the potentials of the electrodes. If such a reaction does not proceed, the difference should be rather small and is due to a change of the activity of mercury as a result of the formation of an amalgam.

Equations 2.10 and 2.11 are valid independently of the form in which a metal exists in the saturated amalgam. It may be present as a soluble intermetallic compound, or such a compound in mercury may be completely dissociated.

When a solid solution of mercury is in the solid metal the sum of the chemical potentials of the metal and mercury in the solid solution[140], should be taken instead of $\mu^o{}_{\text{MeHg}_x}$ in Equation 2.2 This change, however, will have no influence on the final result, and Equation 2.11 will also be valid in such a case.

The validity of Equation 2.11 was confirmed experimentally by Jangg and Kirchmayr. Various metals were investigated, including some that form intermetallic compounds with mercury in the solid phase (manganese) as well as others that do not react with mercury (zinc, lead).

The dependence of the potential of the amalgam on the activity of mercury was also studied.[3,140] The activity of mercury was changed by the introduction of thallium into the amalgam. Because of its very high solubility, thallium changes the activity of mercury considerably. Zebreva et al.[140] investigated the potentials of cadmium amalgams in this way, since thallium does not form intermetallic compounds with cadmium.

Because the potentials of thallium amalgams are more positive than those of cadmium amalgams, the potential of a mixed cadmium-thallium amalgam is determined by the activity of cadmium.

Very good agreement of the experimental results with the expectations based on theoretical equation was found.

Equation 2.11 may also be presented in another form:

$$E^{o}_{Me(Hg)} = E^{o}_{Me} - \frac{\Delta G^{o}}{nF} + \frac{RT}{nF} \ln a_{Me(sat)} + \frac{xRT}{nF} \ln a_{Hg} \qquad (2.12)$$

where $E^{o}_{Me(Hg)}$ denotes the standard potential of the amalgam electrode and $a_{Me(sat)}$ is the activity of the metal in the saturated amalgam. By using the well-known relation between $E^{o}_{Me(Hg)}$ and the polarographic half-wave potential for a reversible process

$$E_{1/2} = E^{o}_{Me(Hg)} + \frac{RT}{2nF} \ln \frac{D_{Me(Hg)}}{D_{Me^{n+}}} \qquad (2.13)$$

one obtains from Equation 2.12

$$E_{1/2} = E^{o}_{Me} - \frac{\Delta G^{o}}{nF} + \frac{RT}{nF} \ln a_{Me(sat)} + \frac{xRT}{nF} \ln a_{Hg} + \frac{RT}{2nF} \ln \frac{D_{Me(Hg)}}{D_{Me^{n+}}} \qquad (2.14)$$

where $D_{Me(Hg)}$ and $D_{Me^{n+}}$ denote the diffusion coefficients of the metal in mercury and the metal ions in the solution.

Since the diffusion coefficients of ions in aqueous solutions and of metals in mercury are not much different, the last term in Equation 2.14 is usually small. In addition, for the amalgam of a metal that is not very soluble in mercury and that does not interact with mercury in the liquid phase, one may assume $a_{Hg} = 1$. These assumptions lead to a simple expression that relates $E_{1/2}$ and E^{o}_{Me}

$$E_{1/2} = E^{o}_{Me} - \frac{\Delta G^{o}}{nF} + \frac{RT}{nF} \ln a_{Me(sat)} \qquad (2.14a)$$

As has already been shown,[138] this expression explains the differences sometimes observed between polarographic half-wave potentials and the standard potentials of the corresponding metal electrodes. According to Equation 2.14a, there are, in general, two reasons for such differences: the interaction of metal with mercury, which is represented by the term $-\Delta G^{o}/nF$, and a failure of the activity of the metal to be equal to unity in a saturated amalgam.

2.2. Application of the Nernst Equation to the Interpretation of the Potentials of Dilute Amalgams

Although the Nernst equation seems to be obeyed by all amalgams at high concentrations, its validity does not extend into the region of very dilute amalgams.

The applicability of the Nernst equation to the interpretations of potentials of electrodes at very low activities of the potential-determining species has been the subject of a number of investigations. Such investigations are facilitated by using metal-amalgam electrodes rather than electrodes prepared by depositing onto the surface of some conductor an amount of metal so small that the activity of the deposited metal is lower than unity.

During investigations of amalgam electrodes, it was found[3,141-144] that deviations from the behavior predicted by the Nernst equation are usually observed if the concentration of metal in the amalgam is below 10^{-5} *M*. Sometimes, especially with more reactive amalgams, the deviations are observed even up to amalgam concentrations of about 10^{-4} *M*, as was found, for instance, for manganese amalgam.[3]

As was pointed out by Zebreva and Kozlovskii, these deviations are due to interactions of the amalgams with the solutions which remain in contact with their surfaces. The metal of the amalgam may be oxidized by oxygen, which is always present at some finite concentration in the solution investigated. Another possibility is a chemical reaction with hydrogen ions or water, which is especially possible with metals having large negative potentials. The metal present in the amalgam may also interact with ions present in the solution having more positive potentials, as was discussed in Section 1.6.

The influence of these reactions on the surface concentration of an amalgam is usually very small when the amalgam is fairly concentrated. Of course, one should be careful to prepare solutions that are as nearly as possible free from oxygen, hydrogen ions, and ions of metals having more positive potentials than the ones being investigated. However, even when such precautions are taken the influences of these side chemical reactions will be significant when the concentration of the metals in the amalgam is small. The decrease of the concentration of the amalgam at the interface between the amalgam and the solution shifts the potential to more positive values than those expected on the basis of the Nernst equation.

The influence of side reactions on the potentials of dilute amalgams was discussed by Losev and co-workers[145] and may be illustrated by the diagrams given in Figure 18.

Line A in this figure represents the dependence on potential of the rate of anodic oxidation of an amalgam having a relatively high and constant concentration. This rate is described by the relation

$$i_a = nFAK^o_{bh}\, a_{Me(Hg)} \exp\, (\beta nFE/RT) \qquad (2.15)$$

Lines K_1 to K_5 correspond to the cathodic process, whose rate is given by

$$i_c = nFAK^o_{fh}\, a_{Me^{n+}} \exp\, (-\alpha nFE/RT) \qquad (2.16)$$

for various concentrations of the metal ion Me^{n+} in the solution. The symbols β and α in Equations 2.15 and 2.16 denote the transfer coefficients for the anodic and cathodic processes, respectively, and the other symbols have their usual significances. It is obvious that the ordinates of the points of intersection of line A with $K_1 \ldots K_5$ will be equal to the equilibrium potentials, and that the abscissas will be equal to the exchange currents.

Line S represents the dependence on potential of the rate of some other cathodic process. This process is a side reaction: it may be the cathodic reduction of oxygen or the reduction of some metal ion with a potential more positive than that of the $Me^{n+}/Me(Hg)$ system.

It follows from Figure 18 that a decrease of the concentration of Me^{n+} may cause the potential to assume a value that is determined by the rate of the anodic reaction and the rate of cathodic side reaction. This potential, corresponding to the point of intersection of lines A and S, will not change with a further decrease of the concentration of Me^{n+}. Under these conditions the validity of the Nernst equation may be investigated by using the procedure proposed by Losev and co-workers.[145] Instead of keeping the concentrations of metal in solution and in the amalgam as independent variables, they proposed to adjust the potential of the electrode and the concentration of metal in one phase (for instance in the amalgam)

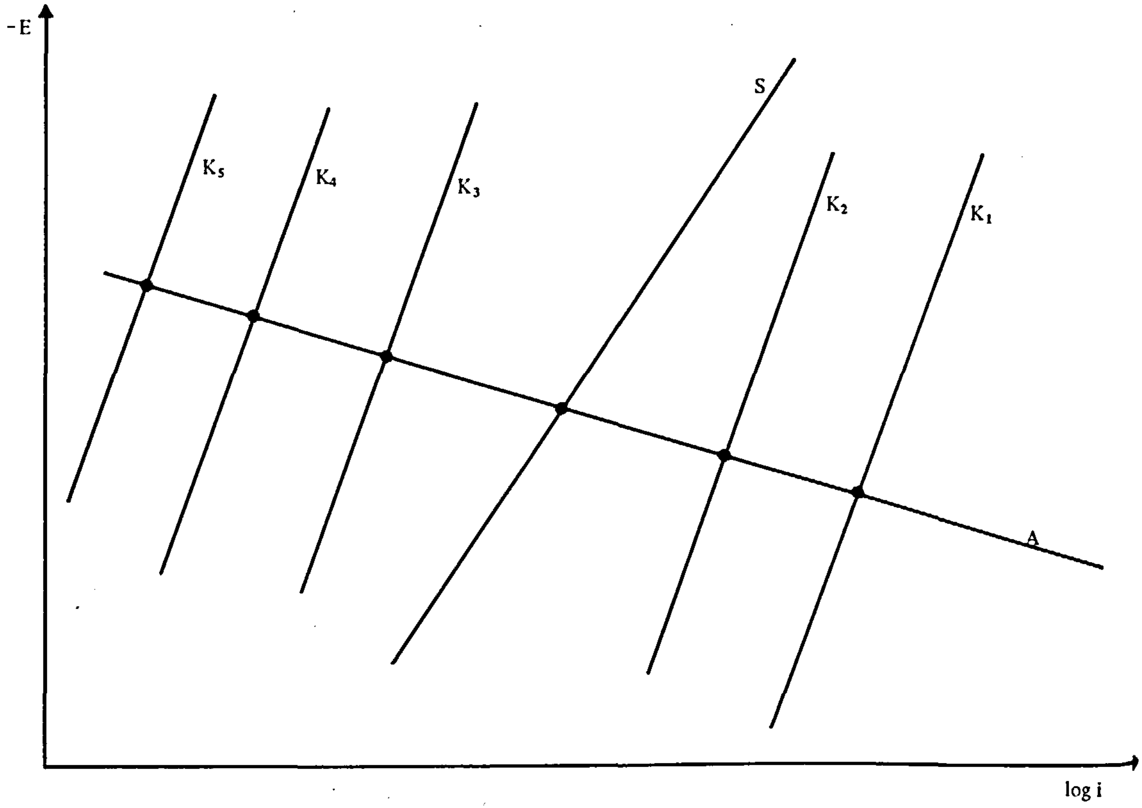

FIGURE 18. Schematic representation of the effects of potential on the rates of some half-reactions.

and measure the equilibrium concentration of the metal in the second phase (for instance in the solution). To determine precisely these low concentrations of metal ions, the radioactive isotopes Mn^{54}, Zn^{65}, and In^{114} were used in their study and gamma-ray spectrometry was applied as a method of analysis. This virtually amounts to using controlled-potential electrolysis to decrease the concentration of the impurity responsible for line S to a level at which it is no longer potential-determining. Using this method it was found that the Nernst equation is obeyed for zinc- and manganese-amalgam electrodes at concentrations of zinc(II) and manganese(II) in the range from 10^{-5} to 10^{-8} *M*. However, the potentials of indium-amalgam electrodes at low concentrations of indium(III) ions in the solution deviated from the behavior expected on the basis of the Nernst equation.

2.3 Potentials of Complex Amalgams

Measurements of the potentials of concentration cells are often used in investigations of the interactions of two or more metals in complex amalgams. Such measurements were published more than 50 years ago by Tammann and Jander,[146] and have since been reported by a number of workers. Their results will be discussed in Section 4. Here we will discuss only the dependence of the e.m.f. of the cell

$$\begin{array}{lll} \text{electrode I} & & \text{electrode II} \\ {}_1\mathrm{Me(Hg)} \,\big|\, {}_1\mathrm{Me}^{n+} & \big| & {}_1\mathrm{Me},\ {}_2\mathrm{Me}\ \text{in Hg} \end{array} \qquad (2.17)$$

on the nature of the interaction of the metals ${}_1\mathrm{Me}$ and ${}_2\mathrm{Me}$ in the complex amalgam. This discussion will follow the idea of Zebreva.[147]

Let us assume that the redox potential of ${}_1\mathrm{Me}$ is more negative than that of either ${}_2\mathrm{Me}$ or mercury. The concentration of this metal in the left-hand electrode is constant throughout the experiment, as is the analytical concentration of ${}_2\mathrm{Me}$ in the second electrode. The concentration of ${}_1\mathrm{Me}$ in the right-hand electrode is changed over a wide range. This metal may be introduced to the amalgam, for instance, by either constant-current or controlled-potential electrolysis.

Four main types of behavior may be considered:

(i) The metals ${}_1\mathrm{Me}$ and ${}_2\mathrm{Me}$ do not interact in mercury. A plot of ΔE against log $[{}_1\mathrm{Me}]_I/[{}_1\mathrm{Me}]_{II}$ is then linear and has a slope equal to 2.3 RT/nF (see curve 1 in Figure 19).

(ii) The metals react to form a freely soluble but weakly dissociated compound in mercury. For simplicity we will assume that this compound has the simple formula ${}_1\mathrm{Me}_2\mathrm{Me}$, and that its dissociation yields ${}_1\mathrm{Me}$ and ${}_2\mathrm{Me}$.

In this case the e.m.f. of the concentration cell (2.17) will be described by the equation

$$\Delta E = \frac{2.3RT}{nF} \log [{}_1\mathrm{Me}]_I - \frac{2.3RT}{nF} \log \frac{K[{}_1\mathrm{Me}_2\mathrm{Me}]_{II}}{[{}_2\mathrm{Me}']_{II}} \qquad (2.18)$$

where $[{}_2\mathrm{Me}']_{II}$ denotes the concentration of free unbound metal in electrode II and K is the dissociation constant of ${}_1\mathrm{Me}_2\mathrm{Me}$.

The results of calculations in which K was taken to be 10^{-3} are shown in Figure 19 (curve 2). If the concentration of ${}_1\mathrm{Me}$ is lower than that of ${}_2\mathrm{Me}$, the curve is parallel to that for a non-reacting system (curve 1) but shifted to an extent that depends on the value of K. At the equivalence point (equal concentrations of the two metals in electrode II) an abrupt change of ΔE is observed, and at high concentrations of $[{}_1\mathrm{Me}]_{II}$ the curve coincides with curve 1.

(iii) The intermetallic compound is only slightly soluble in mercury, and on dissolution it undergoes complete dissociation into simple metals. The potential of electrode II is determined by concentration of ${}_1\mathrm{Me}$, and this in turn is determined by the solubility product of the intermetallic compound.

If the concentrations of metals in the amalgam are so low that the solubility product is not reached, the plot of ΔE against log $[{}_1\mathrm{Me}]_I/[{}_1\mathrm{Me}]_{II}$ (Figure 19, curve 3) coincides with that for a simple, non-reacting amalgam. At higher concentrations, where a precipitate of the compound forms in the amalgam, deviations from curve 1 are observed.

(iv) The intermetallic compound is again only slightly soluble, and the dissolved compound is only partly dissociated. This may be represented by the following scheme

$$[{}_1\mathrm{Me}_2\mathrm{Me}]_{\text{solid}} \leftrightharpoons [{}_1\mathrm{Me}_2\mathrm{Me}]_{\text{liquid}} \leftrightharpoons {}_1\mathrm{Me} + {}_2\mathrm{Me} \qquad (2.19)$$

If the dissociation constant is considerably lower than the solubility product of ${}_1\mathrm{Me}_2\mathrm{Me}$, this case corresponds to *(ii)* for low concentrations of

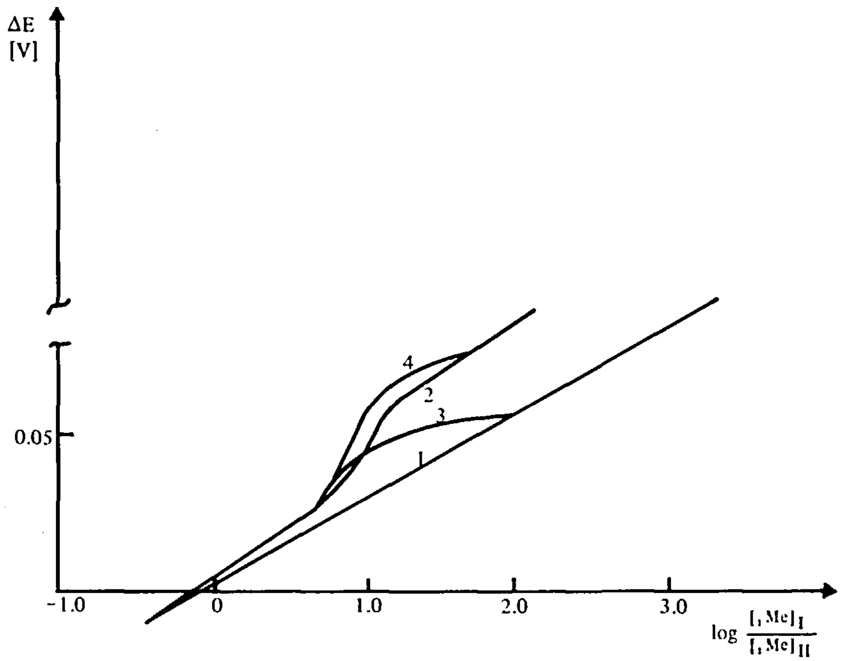

FIGURE 19. Dependence of the e.m.f. of cell (2.17) on the logarithm of the ratio of concentrations of ${}_1$Me in the two electrodes. Curve 1 – the metals do not react; 2 – the compound is soluble in mercury but only partly dissociated; 3 – the compound has only a limited solubility in mercury, but its dissolved part is fully dissociated; and 4 – the compound is only sparingly soluble but is partly dissociated in mercury.

the metals. When the concentrations of the metals suffice to reach the solubility product, the precipitate forms and the dependence of ΔE on log $[{}_1\text{Me}]_I/[{}_1\text{Me}]_{II}$ is shown as curve 4 in Figure 19.

In all of the formulas given above, the indexes I and II denote the corresponding electrodes. It was assumed in these considerations that mercury does not form the compound ${}_1\text{Me}_2\text{MeHg}_x$ with any metal.

It was shown by Lihl and Kirnbauer[148] that mercury does not often form such compounds. However, as was pointed out by Zebreva,[147] even if mercury does interact with the other metals to form ${}_1\text{Me}_2\text{MeHg}_x$, the considerations given above will be unchanged. This is because the concentrations of metals in mercury are usually much lower than the concentration of mercury in liquid mercury (approximately 68 *M*).

3. DETERMINATIONS OF DIFFUSION COEFFICIENTS OF METALS IN MERCURY BY ELECTROCHEMICAL METHODS

Values of diffusion coefficients may give important information about the states and properties of metals dissolved in mercury. Electrochemical methods are sometimes better suited to the determination of these coefficients than classical methods, such as the capillary method, because they may also be applied in investigations of unstable amalgams such as nickel amalgam.

3.1. Electrochemical Methods Used for Determinations of Diffusion Coefficients of Metals in Mercury

Several methods have been used in practice. Many years ago methods were developed[152-154] in which the dependence on time of the potential of an amalgam electrode was used to follow the change of the amalgam concentration brought about by the diffusion of the metal into pure mercury. This is rather complicated, and these methods have fallen into disuse. They have been replaced by other electrochemical methods based on the measurement of a current whose value is proportional to the rate of diffusion of the atoms of investigated metal from the bulk of amalgam to the electrode interface.

One such method is "amalgam polarography," which was first used by Reboul and Bon.[155] They recorded the variation with time of the instantaneous current at a dropping amalgam electrode. The dropping electrode was connected to a horizontal tube of known length filled with mercury. At the other end of the tube an amalgam was introduced. Some time later the current-time characteristics of the dropping electrode began to be affected by the appearance of metal atoms that had diffused through the tube, and the diffusion coefficient could be calculated from the duration of this interval and the geometry of the apparatus.

This method is quite different from the one that is generally known as amalgam polarography and that was first introduced by Lingane[156] and Heyrovsky and Kalousek.[157] It has also been used by several groups of workers to evaluate the diffusion coefficients of atoms dissolved in mercury, most extensively by Furman and Cooper[158] and by Stromberg.[159]

In such investigations dropping amalgam electrodes are used instead of dropping mercury electrodes. Because the concentration of the investigated metal in the amalgam must be precisely known, the method can hardly be used to determine the diffusion coefficients of metals forming amalgams of limited stabilities. Calculations of diffusion coefficients have been based on the Ilkovič equation, both without and with correction for spherical diffusion.[160] This correction is described by the equation (written for the mean current)

$$i_g = 607\, nD_M^{1/2}\, C_M^0\, m^{2/3}\, t_1{}^{1/6} \left[1 - \frac{AD_M^{1/2}\, t_1{}^{1/6}}{m^{1/3}} \right] \tag{3.1}$$

where A = 34 and the other symbols have their generally accepted significances. However, it must be mentioned that Babkin[161] has shown that amalgam polarography leads to results that are unreliable because they depend to some extent on the height of the amalgam reservoir.

Other electroanalytical techniques, such as chronopotentiometry and stationary-electrode voltammetry, may be used in similar ways, but this has not often been done. The latter method has been used occasionally, always in conjunction with the Randles-Ševčik equation or a variant thereof that includes corrections for non-linear diffusion. Since the peak current in stationary-electrode voltammetry depends on the rate of charge transfer as well as the rate of diffusion and is therefore affected by traces of surface-active impurities, this technique does not seem to be well-suited to this purpose. The technique that has been most widely used in recent years is the chronoamperometric oxidation of the metals from the amalgam; it is usually carried out at a potential so positive that the current is controlled by the rate of diffusion of the metal to the amalgam-solution interface, where its concentration is equal to zero. Such experiments are especially easy if they are performed with hanging mercury-drop electrodes of small diameter.

The resulting i-t curves of such anodic oxidation are described by the equation[162]

$$i_g = nFAD_M C_M^0 \left[-\frac{1}{(\pi D_M t)^{1/2}} + \frac{1}{r_0} - \frac{2}{(\pi D_M t)^{1/2}} \sum_{k=1}^{\infty} \exp\left(\frac{-k^2 r_0^2}{D_M t} \right) \right] \tag{3.2}$$

where r_o is the radius of the electrode, A is its surface area, and t is the time of the potentiostatic electrolysis. The second term in Equation 3.2 describes the influence of spherical diffusion, and the last one describes that of the finite diffusion field.

For $t \ll r_o{}^2/D_M$ the last term of Equation 3.2 may be dropped, and then one has

$$i_g = nFAD_M C_M^0 \left[-\frac{1}{(\pi D_M t)^{1/2}} + \frac{1}{r_0} \right] \tag{3.3}$$

In practice, this equation is valid within the error of measurement if the radius of the drop is about 0.5 mm and if the time of electrolysis does not exceed approximately 30 s.

This equation and the procedure for determining the diffusion coefficients of metals in mercury was proposed by Stevens and Shain.[162] According to their suggestion, the chronoamperometric data should be analyzed by plotting $it^{1/2}$ against $t^{1/2}$: as long as Equation 3.3 is obeyed, a straight line should be observed. The slope Δ of this line is equal to $nFAD_M C_M^0/r_o$ and its intercept Z with the $it^{1/2}$ axis is equal to $nFAD_M^{1/2} C_M^0/\pi^{1/2}$. One may easily notice that the ratio of the slope to the intercept gives the value of the diffusion coefficient:

$$D_M = \left(\frac{\Delta r_0}{Z \pi^{1/2}} \right)^2 \tag{3.4}$$

The method proposed by Stevens and Shain is simple and it does not require that the concentration of the amalgam be known, which is important if one investigates unstable amalgams. Only the radius of the electrode has to be precisely known, but this parameter is easily available. Stevens and Shain applied the method to the determination of the diffusion coefficient of cadmium. Using an electrode with a radius of 0.536 mm, they obtained the value 1.61×10^{-5} cm^2 s^{-1} with a deviation of ± 3%.

The method may also be applied when the metal amalgam is produced in the electrolytic cell by the electroreduction of the metal ions at the hanging mercury-drop electrode, as was shown experimentally by Dowgird and Galus.[163]

Another method was developed by Stromberg and Zakharova.[164] This method is based on the recording of anodic voltammetric curves at the HMDE, but employs only the descending part of the curve (at potentials more positive than the peak potential). It is based on the equation given by Chovnyk and Vaschchenko[165] for the potentiostatic oxidation of a metal from a sphere of limited diameter:

$$i = nFC_M^0 D_M 8\pi r_0 \sum_{k=1}^{\infty} \exp\left[-\frac{(k\pi)^2 D_M t}{r_0^2}\right] \tag{3.5}$$

Under typical conditions and for times longer than 10 s, the second and higher terms of the sum may be dropped out with error not exceeding 5%. In addition, making the substitution $nFC_M^0 = q/V$, Equation 3.5 may be transformed into

$$i = A \exp(-BT) \tag{3.6}$$

with

$$A = 8\pi D_M r_0 \frac{q}{V} \tag{3.7}$$

and

$$B = \frac{\pi^2 D_M}{r_0^2} \tag{3.8}$$

where q is the amount of electricity consumed during complete oxidation from the HMDE and V is the volume of the spherical electrode.

It is useful to rewrite Equation 3.6 in logarithmic form:

$$\log i = \log A - \left(\frac{B}{2.3}\right) t \tag{3.9}$$

As follows from this equation, by plotting log i against t, one may easily evaluate the constants A and B from the slope of the resulting straight line and its intercept with the log i axis at t = 0. The diffusion coefficient may be calculated from the values of A and B if the experimental conditions obeyed the theoretical assumptions.

This general technique may be applied not only to the analysis of chronoamperometric curves at longer electrolysis times but also to the ascending parts of voltammetric curves for the oxidations of metals from the HMDE. These curves should be recorded in such a way that the process is controlled by steps occurring after the charge transfer. This requirement may be fulfilled (for fast electrode reactions) if the concentration of the metal ions in the solution is large and if a quite positive potential, at the foot of the cathodic voltammetric peak, is applied in the reduction process. If after the electroreduction, the reduced metal diffuses into the HMDE, the cathodic current is given by[50]

$$\begin{aligned} i = {} & nFAD_M^{1/2} C_{ox}^0 \exp\left[\frac{nF(E^0 - E)}{RT}\right]\left[\frac{1}{(\pi t)^{1/2}} \sum_{k=-\infty}^{k=+\infty} \exp\left(\frac{k^2 r_0^2}{tD_M}\right) - \frac{D_M^{1/2}}{r_0}\right] = \frac{nFAD_M}{r_0} C_{ox}^0 \\ & \cdot \exp\left[\frac{nF(E^0 - E)}{RT}\right] \sum_{k=1}^{\infty} \exp\left(-\frac{k^2\pi^2 D_M t}{r_0^2}\right) \end{aligned} \tag{3.10}$$

Assuming that $t << r_o^2/D_M$, one arrives at the dependence

$$i = nFAD_M^{1/2} C_{ox}^0 \exp\left[\frac{nF(E^0 - E)}{RT}\right]\left[\frac{1}{(\pi t)^{1/2}} - \frac{D_M^{1/2}}{r_0}\right] \tag{3.11}$$

This equation may be used to determine the diffusion coefficient from chronoamperometric experiments, using, as did Stevens and Shain, the plot of $it^{1/2}$ against $t^{1/2}$.

When $t >> r_0^2/D_M\pi$, the current is given by

$$i = \frac{nFAD_M C_{ox}^0}{r_0} \exp\left[\frac{nF(E^0 - E)}{RT}\right] \exp\left[-\frac{\pi^2 D_M t}{r_0^2}\right] \tag{3.12}$$

The application of Equation 3.11 has the advantage over the procedure of Stevens and Shain that the duration of the experiment is shorter. One need only record the i-t curve at the foot of the wave for several seconds. If the experiment is more prolonged, the i-t curve may be analyzed on the basis of Equation 3.12. A plot of log i against t should then be constructed and should be a straight line; the diffusion coefficient may be calculated by combining the value of the slope with that of $it^{1/2}$ at t = O. These procedures were used by Barański[50] to evaluate the diffusion coefficient of nickel in mercury.

One should stress, however, that methods based on the application of the HMDE will not give reliable results when applied to the determination of diffusion coefficients in mercury of alkali or alkali earth metals. This is because experiments carried out in the writer's laboratory have shown that the anodic i-t curves of such amalgams are deformed by the presence of maxima. These parasitic effects disappeared when a mercury-film electrode was used instead of the HMDE. A mercury film on a copper base was used in the experiments performed by Fitak.[166]

For the oxidation of a metal from such an electrode, if the potential of oxidation is sufficiently positive that the process is controlled uniquely by the rate at which the metal diffuses from a thin layer of amalgam to the interphase, the current recorded under chronoamperometric conditions is

$$i = 2nFAC^0_M \frac{D_M}{\pi l} \sum_{k=1}^{\infty} \exp \left[\left(\frac{\pi D_M}{4 l^2} \right) (2K - 1)^2 t \right] \tag{3.13}$$

where l is the thickness of the amalgam layer, which must be known. For long electrolysis times, when $t \gg 4l^2/\pi D$, Equation 3.13 may be simplified to

$$i = 2nFAC^0_M \frac{D_M}{\pi l} \exp \left(- \frac{\pi D_M t}{4l^2} \right) \tag{3.14}$$

The analysis of experimental data should be carried out by plotting log i against t:

$$\log i = \log 2nFAC^0_M D_M/\pi l - \pi D_M t/9.2 l^2 \tag{3.15}$$

Such a plot should be linear, and the diffusion coefficient may be determined from its slope. The required value of l may be determined by a similar analysis of data for a metal whose diffusion coefficient in mercury is known with good accuracy.

3.2 Values of Diffusion Coefficients Obtained by Electroanalytical Techniques

This section will present mainly the diffusion coefficients determined by electroanalytical methods, but some results obtained by non-electrochemical methods will also be given for the sake of comparison. From results obtained by electrochemical methods, the chief attention is given to those secured recently, mainly by the analysis of i-t curves for the oxidations of metals from the HMDE. These methods seem to be more reliable than, for instance, amalgam polarography. The method proposed by Stevens and Shain[162] has been the most widely used. To check the validity of this method, Dowgird[163,167] has studied the diffusion coefficients of zinc, cadmium, and lead in our laboratory. Amalgams of these metals were produced by electroreductions of their ions at the HMDE. Hanging electrodes of various sizes with diameters ranging from 0.34 to 0.63 mm, were used.

For cadmium, plots of $it^{1/2}$ against $t^{1/2}$ were always linear. Figure 20 shows a typical plot of this sort. Using hanging electrodes of larger diameters, the reproducibility of the results was found to be good, and the value of 1.53×10^{-5} $cm^2\ s^{-1}$ was obtained, for the diffusion coefficient lies between the values obtained by

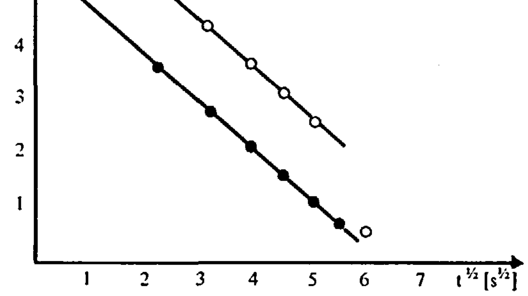

FIGURE 20. Plots of $it^{1/2}$ against $t^{1/2}$ for the anodic oxidation of cadmium amalgam.

Stromberg and by Shain (Table 7). A lower value was obtained from measurements carried out with a hanging-drop electrode with a radius of 0.34 mm.

Very good agreement of diffusion coefficients was observed for lead, though the electrodes used had various diameters. These values are in excellent agreement with the one reported by Stromberg and Zakharova.[164]

A large discrepancy was observed in the determination of the diffusion coefficient of zinc. Using small electrodes (radius = 0.34 mm) there was practically no linear segment of a plot of $it^{1/2}$ against $t^{1/2}$, while with larger electrodes the value determined was dependent on the radius of the electrode, and a practically constant value was found only with electrodes having diameters of the order of 0.6 mm.

One may conclude that this method will give reliable results only if the radius of the electrode is sufficiently large – or, speaking more strictly, when the ratio r_0/D is sufficiently large. It follows from these investigations that this ratio should exceed about 3×10^3 s cm^{-1}. It should be remembered, however, that this ratio should not be too large, because this method for the determination of diffusion coefficients is based on the effect of spherical diffusion. With a very large electrode, decrease of the current due to sphericity becomes small in comparison to the total current, and the precision that can be attained in the determination of a diffusion coefficient decreases substantially. On the other hand, if the electrode is too small, the condition of a large diffusion field is not fulfilled and Equation 3.3 is no longer valid. Then the linear part of a plot of $it^{1/2}$ against $t^{1/2}$ is too short to lead to proper results, as is the case with zinc.

Fitak[166] has used this method to determine the diffusion coefficients of many metals in mercury. His results agree satisfactorily with some other values given in the recent literature, and are given, together with the results of other workers, in Table 8, which in many cases also includes values selected by the writer as representing the best estimates that can be made in the light of our present knowledge.

Once more I should like to stress that the most reliable results are those obtained with the HMDE, especially when the oxidation from the hanging drop was carried out under potentiostatic conditions.

The results of Zakharov[178] are obtained by calculations and will be briefly discussed below. These values are generally too low.

Inspection of the table shows that further work is needed with amalgams of the alkali metals and alkaline earth metals, for which the existing data do not suffice to point to any particular value as being correct and (especially for the alkaline earth metal amalgams) are not in acceptable agreement. Some new electrochemical techniques should be developed, and new electrodes seem especially to be needed. Fitak et al.[187] tried to make progress in this respect, but the results were not very good: further work should be carried out to develop mercury electrodes that would be applicable to determinations of the diffusion coefficients of the alkali and alkaline earth metals in mercury. Such determinations should be carried out in the future in non-aqueous solvents.

Especially large differences between the results are observed with manganese and nickel, for which the results obtained in our laboratory are much lower than those reported by other workers. One should stress, however, that we repeated our experiments many times, reaching results similar to those reported in Table 8. In particular, the

TABLE 7

Diffusion Coefficients of Cadmium, Lead, and Zinc Obtained by Chronoamperometric Methods

Diffusion coefficient × 10^5 (cm^2 s^{-1})

	r_o (mm)						
Metal	0.34	0.43	0.54	0.59	0.63	Stromberg and Zakharova,[164] $r_o = 0.38$ mm	Stevens and Shain,[162] $0.52 \leq r_o \leq 0.75$ mm
Cd	1.45	1.53	1.54	–	–	1.45	1.61
Pb	1.19	1.16	1.17	–	–	1.17	–
Zn	–	1.74	1.88	1.98	2.01	1.58	–

TABLE 8

Diffusion Coefficients of Metals in Mercury Determined by Electrochemical Methods

Metal	Authors	Method	Temperature	Diffusion coefficient $D \times 10^5$ ($cm^2\ s^{-1}$)
Zn	Meyer[152]	EMF	15	2.42
	von Wogau[154]	EMF	8.0–14.3	2.52
	Schwarz[169]		25	2.4
	Weischedel[170]		20	1.67
	Stromberg[159]	pol.	25	1.57
	Stromberg and Zakharova[164]	HMDE	25	1.58
	Furman and Cooper[158]	pol.	25	1.67
	Chovnyk and Vashchenko[165]	HMDE	20	3.15
	Sagadieva[26]	pol.	20	2.1
	Gao Khun[176]	HMDE	20	1.68
	Krasnova et al.[177]	HMDE	25	2.2 ± 0.2
	Dowgird and Galus[163]	HMDE	25	2.0
	Fitak[166]	HMDE	25	1.89
	suggested value		25	1.90
Cd	Meyer[152]	EMF	15	1.81
	von Wogau[154]	EMF	8.7	1.68
	Cohen and Bruins[153]	EMF	20	1.52
	Weischedel[170]	electr. conduct.	20	1.53
	Stromberg[159]	pol.	25	2.07
	Stromberg and Zakharova[164]	HMDE	25	1.45
	Furman and Cooper[158]	pol.	25	1.52
	Chovnyk and Vashchenko[165]	HMDE	20	2.45
	Schwarz[169]		25	2.0
	Stackelberg and Toome[168]	pol.	22	1.66
	Sagadieva[26]	pol.	20	2.7
	Gao Khun[176]	HMDE	20	1.51
	Krasnova et al.[177]	HMDE	25	2.0 ± 0.4
	Turner and Winkler[173]		20	1.52
	Dowgird and Galus[163]	HMDE	25	1.53
	Fitak[166]	HMDE	25	1.42
	Zakharov[178]	calcul.	20	0.92
	Barański and Galus[61]	HMDE	25	1.50
	suggested value		25	1.52
Cu	Furman and Cooper[158]	pol.	25	1.06
	Stromberg and Zakharova[164]	HMDE	25	0.93
	Zebreva		20	1.04 ± 0.05
	Sagadieva[26]	pol.	19	1.2
	Gao Khun[176]	HMDE	20	0.88
	Fitak[166]	HMDE	25	1.19
	Zakharov[178]	calcul.	20	1.08
	suggested value		25	1.06
Tl	von Wogau[154]	EMF	11.0–12.0	1.03
	Furman and Cooper[158]	pol.	25	0.99
	Stromberg[159]	pol.	25	1.60
	Stromberg and Zakharova[164]	HMDE	25	1.03
	Schwarz[169]		25	1.18
	Sagadieva[26]	pol.	18	1.1
	Gao Khun[176]	HMDE	20	1.05
	Fitak[166]	HMDE	25	0.91
	Zakharov[178]	calcul.	20	0.82
	suggested value		25	1.0

TABLE 8 *(continued)*

Diffusion Coefficients of Metals in Mercury Determined by Electrochemical Methods

Metal	Authors	Method	Temperature	Diffusion coefficient $D \times 10^5$ ($cm^2\ s^{-1}$)
Sn	von Wogau[154]	EMF	9.6–14.0	1.80
	Furman and Cooper[158]	pol.	25	1.68
	Stromberg and Zakharova[164]	HMDE	25	1.30
	Schwarz[169]		25	1.5
	Gao Khun[176]	HMDE	20	1.46
	Alikina[179]		30	1.30
	Fitak[166]	HMDE	25	1.48
	suggested value		25	1.48
In	Stromberg and Zakharova[164]	HMDE	25	1.31
	Stackelberg and Toome[168]	pol.	22	1.47
	Sagadieva[26]	pol.	19	1.8
	Gao Khun[176]	HMDE	20	1.42
	Alikina[179]		30	1.55
	Fitak[166]	HMDE	25	1.36
	suggested value		25	1.36
Pb	Meyer[152]	EMF	15.6	1.58
	von Wogau[154]	EMF	9.0–10.0	1.74
	Furman and Cooper[158]	pol.	25	1.16
	Stromberg[159]	pol.	25	1.39
	Stromberg and Zakharova[164]	HMDE	25	1.17
	Schwarz[169]		25	2.1
	Chovnyk and Vashchenko[165]	HMDE	20	1.9
	Stackelberg and Toome[168]	pol.	22	1.40
	Gao Khun[176]	HMDE	20	1.25
	Turner and Winkler[173]	pol.	20	1.28
	Fitak[166]	HMDE	25	1.25
	Zakharov[178]	calcul.	20	0.79
	Dowgird and Galus[163]	HMDE	25	1.17
	suggested value		25	1.17
Bi	Furman and Cooper[158]	pol.	25	0.99
	Stromberg[159]	pol.	25	1.62
	Stromberg and Zakharova[164]	HMDE	25	1.24
	Schwarz[169]		25	1.5
	Gao Khun[176]	HMDE	20	1.35
	Zakharov[178]	calcul.	20	0.75
	Nigmatullina[13]		20	1.4
	Fitak[166]	HMDE	25	1.44
	suggested value		25	1.44
Sb	Stromberg and Zakharova[164]	HMDE	25	1.40
	Gao Khun[176]	HMDE	20	1.47
	Toibaev[181]		20	1.3
	Fitak[166]	HMDE	90	2.4
Mn	Sagadieva[26]	pol.	17	3.1
	Krasnova et al.[177]	HMDE	25	1.9 ± 0.2
	Gao Khun[176]	HMDE	20	1.84
	Lange and Bukhman[182]		20	1.2
	Dowgird and Galus[163]	HMDE	25	0.90 ± 0.08
	Fitak[166]	HMDE	25	0.94
	suggested value		25	0.94

TABLE 8 (continued)

Diffusion Coefficients of Metals in Mercury Determined by Electrochemical Methods

Metal	Authors	Method	Temperature	Diffusion coefficient $D \times 10^5$ ($cm^2\ s^{-1}$)
Ni	Krasnova et al.[177]	HMDE	25	2.0 ± 0.3
	Dowgird and Galus[163]	HMDE	25	0.65 ± 0.03
	Barański and Galus[61]	HMDE	25	0.54
	Fitak[166]	HMDE	25	0.64
	suggested value		25	0.65
Ge	Stromberg and Zakharova[185]		25	1.70
	Gao Khun[176]	HMDE	20	1.71
Ag	Schwarz[169]		25	1.0
	Stromberg and Zakharova[185]		25	0.9
Au	Schwarz[169]		25	0.73
	Stromberg and Zakharova[185]		25	0.6
	Austen[184]			0.83
Hg	Nachtrieb and Petit[172]	isotope Hg^{203}	20	1.5
	Hoffman[171]	isotope Hg^{203}	25	1.83
Ga	Stromberg and Zakharova[164]	HMDE	25	1.57
	Gao Khun[176]	HMDE	20	1.64
	Fitak[166]	HMDE	25	1.72
	suggested value		25	1.6
Li	von Wogau[154]	EMF	8.2	0.76
	Schwarz[169]		25	0.93
Na	von Wogau[154]	EMF	8.2	0.74
	Schwarz[169]		25	0.86
	Stackelberg and Toome[168]	pol.	22	0.80
	Gao Khun[176]	HMDE	20	0.76
	Fitak[166]	film electrode	25	0.97
K	von Wogau[154]	EMF	10.5	0.61
	Schwarz[169]		25	0.61
	Gao Khun[176]	HMDE	20	0.66
	Fitak[166]	film electrode	25	0.85
Rb	von Wogau[154]	EMF	7.3	0.53
	Fitak[166]	film electrode	25	0.75
Cs	von Wogau[154]	EMF	7.3	0.52
	Schwarz[169]		25	0.65
	Fitak[166]	film electrode	25	0.54
Ca	von Wogau[154]	EMF	10.2	0.62
Sr	von Wogau[154]	EMF	9.4	0.54
	Gao Khun[176]	HMDE	20	1.08
Ba	von Wogau[154]	EMF	7.8	0.60
	Gao Khun[176]	HMDE	20	1.04
	Fitak[166]	film electrode	25	0.49

diffusion coefficient of nickel was redetermined many times by Barański,[50] who used the various chronoamperometric procedures discussed in Section 3.1. It seems that the very high value of the diffusion coefficient of nickel reported by Krasnova et al.[177] is due to an incorrect analysis of their experimental data.

The diffusion coefficients of nickel and cadmium in mercury were also determined at higher temperatures, using chronoamperometric oxidation of amalgams and the procedure of Stevens and Shain. The results obtained are given in Table 9, together with the radius of the diffusing species as calculated from the Stokes-Einstein equation. In the case of cadmium, the radius calculated from the diffusion coefficient agrees with the ionic radius of Cd^{2+}, but for nickel it is several times as large as the radius of the Ni(II) ion and is also considerably larger than the radius of the nickel atom. From a plot of log D against 1/T for nickel, the enthalpy of activation for the diffusion of nickel in mercury was calculated and found to be equal to 1300 cal mol^{-1}.

3.3. Correlations and Conclusions

Inspection of Table 8 shows that the diffusion coefficients of metals in mercury differ rather widely. The lowest values are those for the alkali and alkaline earth metals. This suggests that there is a correlation between the value of the diffusion coefficient of a metal and its nature. Wogau[154] long ago noticed that diffusion coefficients vary periodically with the atomic weight. Obviously, the metals with larger atomic volumes were found to have smaller diffusion coefficients.

TABLE 9

Temperature Dependences of the Diffusion Coefficients of Nickel and Cadmium in Mercury

	Ni		Cd	
Temperature (°C)	D × 10^6 (cm^2 s^{-1})	r_0(A)	D × 10^6 (cm^2 s^{-1})	r_0(A)
25	5.4	3.97	15.0	1.42
55	6.2	4.23	16.5	1.57
70	6.8	4.20	19.0	1.50
105	7.8	4.35	23.0	1.48
125	8.7	4.27	24.0	1.54
150	9.4	4.36	25.0	1.65
184	10.5	4.42	29.0	1.60
205	11.6	4.29		
230	12.0	4.50		

Cooper and Furman[158] briefly discussed this and correlations proposed by other workers, and they also studied the relation between the diffusion coefficients of metals in mercury and the atomic radii of the metals. Only the diffusion coefficients of copper and bismuth, of the seven metals studied, deviated significantly from a line that represented the diffusion coefficients of the other metals. On the basis of those deviations, the formation of compounds between mercury and copper and between mercury and bismuth was suggested.

However, their correlation is of only limited value, since the relation between the diffusion coefficient and the radius of the metal is not linear. This follows from the Stokes-Einstein equation, which in general form is

$$D = kT/K\pi\eta r \qquad (3.16)$$

where k is the Boltzmann constant, η is the viscosity of mercury, and r is the radius of the diffusing particle. K is a constant, which in the calculations of several authors[178,185,186] was taken as equal to 6.

Zakharov[178] calculated the diffusion coefficients of metals in mercury from Equation 3.16 and obtained values too low in comparison with those found experimentally. Stromberg and Zakharova[185] have also calculated diffusion coefficients of 7 metals, using atomic radii, that are from 56 to 75% lower than the corresponding experimental values. Better agreement was found when the radii of low-valency ions were used in the calculations.

Gladyshev[186] also used ionic radii in calculations of D on the basis of Equation 3.16. Although in several cases the experimental and calculated values were found to be in good agreement, it should be said that the valency of the metal ions in the amalgam state was sometimes assumed quite arbitrarily.

For the alkali metals, calculations based on the ionic radii (valency +1) gave values that exceeded the experimental ones, which led[186] to the conclusion that these metals diffuse in mercury as ionic solvates. This is also true for the alkaline earth metals. The fact that the experimental values of the diffusion coefficients of copper, silver, and gold are also lower than the calculated ones may suggest[186] that these metals also diffuse as ionic metal solvates of the type $MeHg^+$.

However, another interpretation may be given[50,166,187] As was shown by McLaughlin,[188] the coefficient K in the Stokes-Einstein equation should be taken as equal to 6 only if the dimensions of the diffusing particles significantly exceed those of solvent molecules.

If the dimensions of the diffusing substance and the solvent molecules are similar, this coefficient should be approximately equal to 4. With K = 6, earlier authors had used ionic radii in order to obtain larger values of the diffusion coefficients that were closer to experimental values, but with K = 4 *in Equation 3.16, one obtains* good agreement between the calculated and experimental values for a number of metals (lead, zinc, cadmium, bismuth, gallium, antimony, and tin) using metallic radii (Figure 21). This would imply that these metals diffuse nonsolvated by mercury.

It seems that this correlation with metallic radii is more reasonable, since it would be surprising if the dimensions of diffusing particles were equal to those of the corresponding ions in ionic crystals.

The diffusion coefficients of the alkali, alkaline earth, and copper-group metals and manganese, nickel, and thallium are lower than those calculated from their metallic radii. This discrepancy may be attributable to the formation of solvates or intermetallic compounds. The existence of such species has been reported for almost all of these metals (see Sections 1 and 2). It should be added that the diffusion coefficients of the alkali metals are quite close to a straight line on a plot of 1/D against r, and that the extrapolation of this line to r = 0 gives an intercept whose value is close to the *reciprocal of that of the self-diffusion coefficient* of mercury. This suggest that for the alkali metals the diffusing molecules are compounds of these metals with mercury which have the composition MeHg.

In conclusion, it may be said that values of diffusion coefficients give much information concerning the natures of metals dissolved in mercury. This is especially important in the case of diluted amalgams.

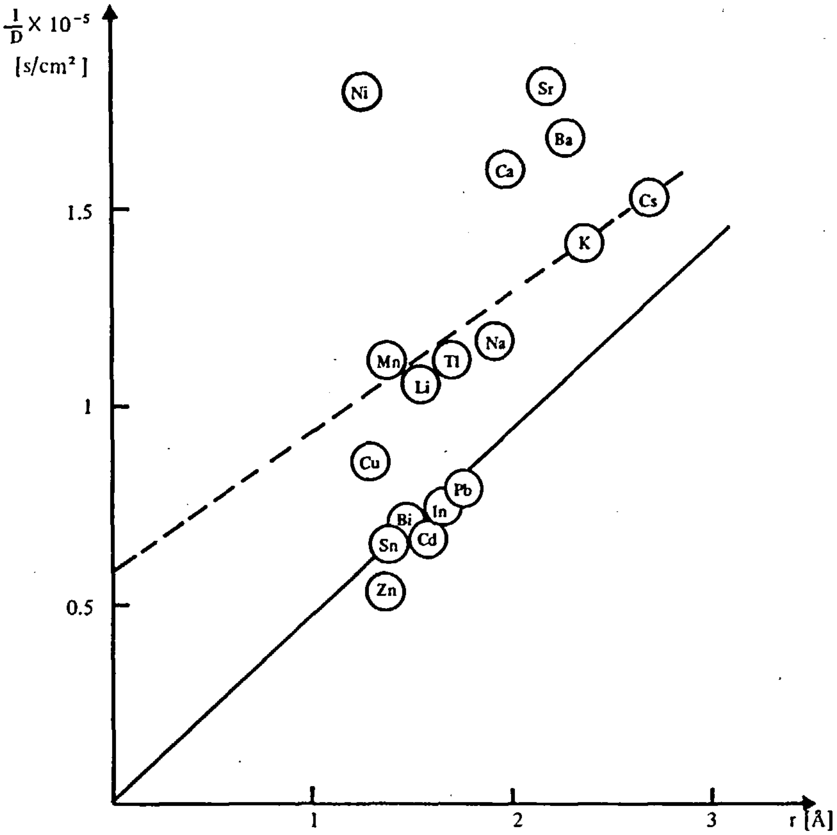

FIGURE 21. Dependence of 1/D on the metallic radius for atoms of the metals that have been investigated.

4. ELECTROCHEMICAL INVESTIGATIONS OF COMPLEX AMALGAMS

The chemical reactions that occur between metals dissolved in mercury have been studied by many workers in recent years. These studies have been oriented mainly to determinations of the compositions and thermodynamic parameters of the intermetallic compounds that are formed by such reactions. The results obtained are important for the anodic stripping methods, which are widely applied in analysis.[189,190] These methods are based on the electrolytic deposition and accumulation of metals, usually in mercury electrodes of small volume. If the deposited metals interact in the mercury, the currents that are measured in the oxidation step are not proportional to the contents of these metals in the samples analyzed. Consequently, a knowledge of the natures of such reactions and of their rates and equilibrium constants is important from the points of view of both pure and applied chemistry.

In such investigations, electrochemical methods have already played a very important role, and it is the author's belief that with the development of these methods, their importance should become even more predominant in the future.

4.1. Electrochemical Methods for the Investigation of Intermetallic Compounds Formed in Mercury

Several electrochemical methods have been used in the study of complex amalgams. This review presents the ones that are the most important and most widely used.

4.1.1. Potentiometry

This method was applied to the study of the formation of intermetallic compounds in mercury by Tammann and co-workers[146] many years ago, and since then it has often been used by various people. Some of its applications will be discussed further in this section.

In principle, this method of investigating the formation of intermetallic compounds resembles the potentiometric titration of one substance by another. An amalgam of one metal $_1Me$ which is originally present in mercury is titrated with the second metal $_2Me$, which reacts with $_1Me$ to form the intermetallic compound. If the redox potential of $_2Me$ is more negative than that of $_1Me$, then the potential of an amalgam electrode containing both metals is determined by the redox couple $_2Me^{n+}/_2Me(Hg)$.

As the concentration of $_2Me$ in the amalgam increases, the concentration of $_1Me$ drops as a result of the reaction

$$_1Me(Hg) + m\,_2Me(Hg) \leftrightharpoons {}_1Me_2Me_m(Hg) \qquad (4.1)$$

Increasing the amount of $_2Me$ in the amalgam is usually done either by adding known amounts of $_2Me$ amalgam or by electrodepositing this metal at the $_1Me$-amalgam electrode, usually with a constant current.

A general discussion of the various shapes of the resulting potentiometric curves and their dependence on the nature of the reaction was presented by Zebreva, and her considerations are briefly summarized in Section 2.3. Stromberg and Belousov[191,192] recently considered these problems in greater detail. Two cases were discussed. The first is that in which Reaction 4.1 yields an intermetallic compound, $_1Me_2Me_m$, that is sparingly soluble in mercury. For this case, they derived[191] the following equation of the potentiometric curve

$$A\beta/\alpha = [1 - m\,(1 - \alpha)/\beta]^m \qquad (4.2)$$

where

$$-\log\alpha = nF(E - E_0)/2.3RT \qquad (4.3)$$

and

$$\beta = [_2Me]/[_1Me] \qquad (4.4)$$

$$A = K_{so}/[_2Me]^{m+1} \qquad (4.5)$$

where K_{so} is the solubility product of the compound $_1Me_2Me_m(Hg)$; $[_1Me]$ and $[_2Me]$ are the analytical concentrations of $_1Me$ and $_2Me$, respectively, in the amalgam; and E_0 and E denote the potentials of the amalgam electrode in the absence and presence of the second metal $_2Me$, respectively.

Stromberg and Belousov[192] also considered the shape of the potentiometric curve that is obtained when Reaction 4.1 yields a compound that is soluble in mercury and is in dissociative equilibrium with the free metals according to Equation 4.1. In this case, the theoretical shape of the potentiometric curve will be described by the equation

$$-B(1-\alpha)/\alpha = [1 - m(1-\alpha)/\beta]^m \tag{4.6}$$

with

$$B = 1/K\,[_2Me]^m \tag{4.7}$$

where K is the stability constant of $_1Me_2Me_m$ and α and β are given by Equations 4.3 and 4.4.

Using these results, Stromberg and coworkers[193] proposed procedures for determinations of the thermodynamic parameters of intermetallic compounds.

By introducing the dimensionless parameters W, U, and V, defined by

$$W = (1-\alpha)/\alpha$$

$$V = (1-\alpha)/\beta$$

and

$$U = W/V = \beta/\alpha$$

Equation 4.6 may be transformed into

$$BW = (1 - mV)^m \tag{4.8}$$

while Equation 4.2 will become

$$AU = (1 - mV)^m \tag{4.9}$$

Various approaches were proposed. At first, a plot of U against V should be constructed from the data. On this plot one locates two values of U (U_1 and U_2) such that $U_2 = 2U_1$, and finds the corresponding values of V_1 and V_2. On the basis of Equation 4.9, one may write

$$AU_1 = (1 - mV_1)^m \text{ and } 2AU_1 = (1 - mV_2)^m \tag{4.10}$$

from which one can obtain

$$V_2 = aV_1 - b \tag{4.11}$$

where

$$(a-1)/b = m \tag{4.12}$$

Taking several values of U_1 and $2U_1$, and finding the corresponding values of V_1 and V_2, one may construct a plot of V_2 against V_1. It follows from Equation 4.11 that such a plot should be linear, and values of a and b are easily obtained, whereupon m may be calculated with the help of Equation 4.12. Using m, U_1, V_2, and Equation 4.10, one may easily calculate A and subsequently, by applying Equation 4.5, the solubility product K_{so}.

Another procedure has also been advised.[193] From Equation 4.9, one can obtain

$$\log U = -\log A + m \log (1 - mV) \tag{4.13}$$

Assuming some arbitrary value of m, one constructs a plot of log U against log (1 - mV). If it is a straight line with a slope equal to the assumed value of m, then that value of m describes the composition of the intermetallic compound, and in addition the intercept of the line on the log U axis [where log (1 - mV) = 0] is equal to -log A. If the slope of the line does not agree with the assumed value of m, another value of m has to be assumed until the proper one is found by trial and error. These procedures were used by Stromberg et al. to recalculate the solubility product of AuZn in mercury using the potentiometric data of Hartmann and Schölzel.[194]

This procedure may be greatly simplified by using hanging amalgam-drop electrodes.[195] For instance, one may use such an electrode filled with gold amalgam and employ electrolytic deposition to add a second metal that will react with gold to form an intermetallic compound. This procedure has been worked out with the reaction of gold and zinc studied earlier.[194] The experiments were carried out with hanging-drop electrodes of gold amalgam and mercury. The same amount of zinc was deposited into each of the two electrodes, using constant-current electrolysis. The potentials of the electrodes were measured at various times after the deposition was stopped. The results of typical measurements are shown in Figure 22. For each electrode significant changes of potential were observed during approximately the first minute after electrolysis; these reflect the finite rates both of gold-zinc interaction and of the attainment of uniform distribution of the various

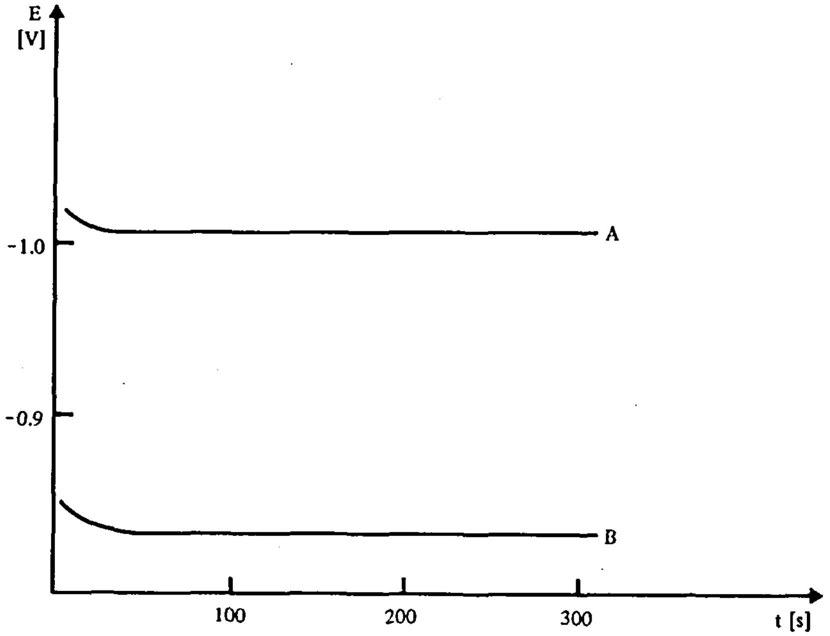

FIGURE 22. Variation with time of the potentials of hanging-drop electrodes containing (A) mercury and (B) 0.05 *M* gold amalgam. The amount of zinc introduced into each electrode was 4.27 mC, and the concentration of zinc(II) in the solution was 0.10 *M*.

species in the solution and in the mercury phase. For several minutes thereafter, the changes of potential were small and linear with time. To simplify the calculations and to increase the precision, the calculations were based on the difference between the potentials of two electrodes (gold amalgam and mercury) into which equal amounts of zinc had been deposited by cathodic electrolysis for the same time and with the same current. Since the potentials of the electrodes changed slowly due to corrosion, the potentials were extrapolated to $t = 0$, and these extrapolated values were used in further calculations. This was expected to yield reliable results because the reaction of gold with zinc in mercury is fast, and the equilibrium was therefore reached in the more concentrated amalgams within the period of time that was necessary to reach uniform distribution.

The dependence of the difference ΔE between the potentials of the mercury and gold-amalgam electrodes on the amount of zinc introduced into the drop is shown in Figure 23. In every case the jump of ΔE was observed at the point where the Au-Zn ratio was equal to one, indicating that the formula of the compound is AuZn. From this formula and the experimental values of ΔE, the thermodynamic parameters of the studied compound could easily be calculated.

This technique is very simple and may be easily applied if the reaction between the metals in the mercury phase is sufficiently fast.

4.1.2 Amalgam Polarography

Amalgam polarography has been applied to the study of the formation of intermetallic compounds in mercury, as for instance in the work of Zebreva and Kozlovskii[196] on the formation of CuZn in the Cu-Zn-Hg system.

In such investigations it is customary to prepare several complex amalgams that contain the same analytical concentration of one metal but various concentrations of the second one, and to examine the polarograms of these amalgams. The results may be analyzed by constructing a plot of the anodic limiting current of one metal against the ratio of the concentrations of the two metals in the amalgam. Such a plot is similar in nature and shape to the well-known amperometric titration plot.

The shapes of the expected curves are presented schematically in Figure 24. The two line segments

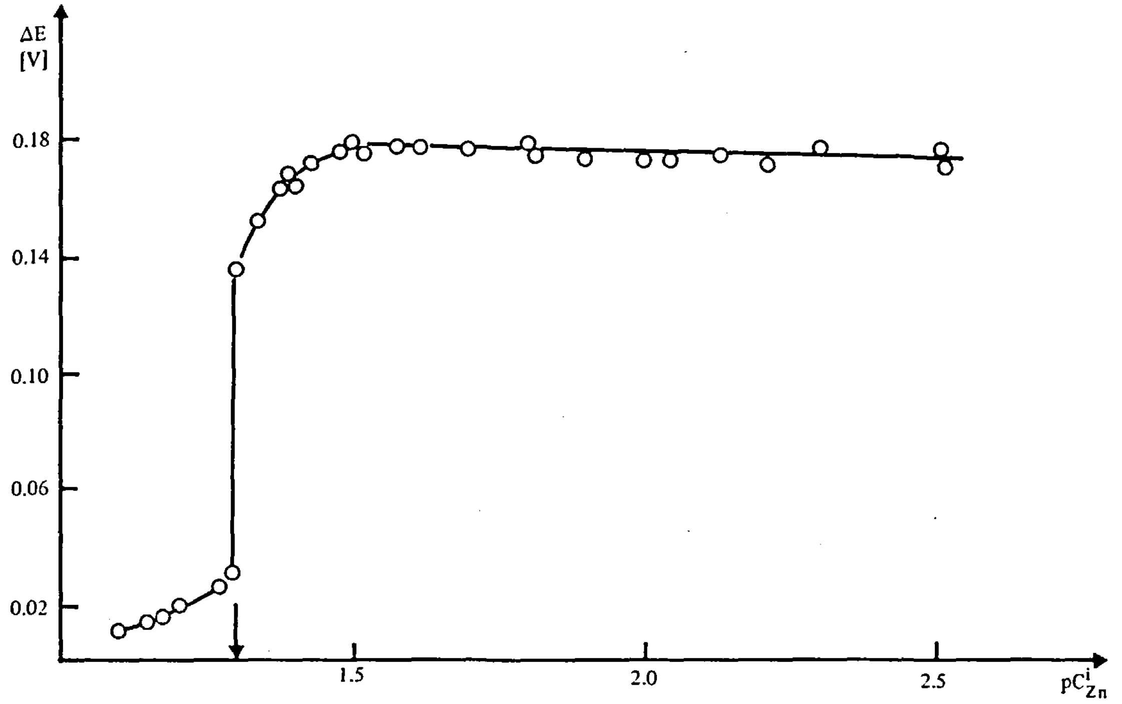

FIGURE 23. The variation of the difference between the potentials of mercury and 0.05 *M* gold amalgam electrodes containing deposited zinc with the logarithm of the initial concentration of zinc (C^i_{Zn}) in the electrode. The arrow corresponds to equal concentrations of gold and zinc in the mercury.

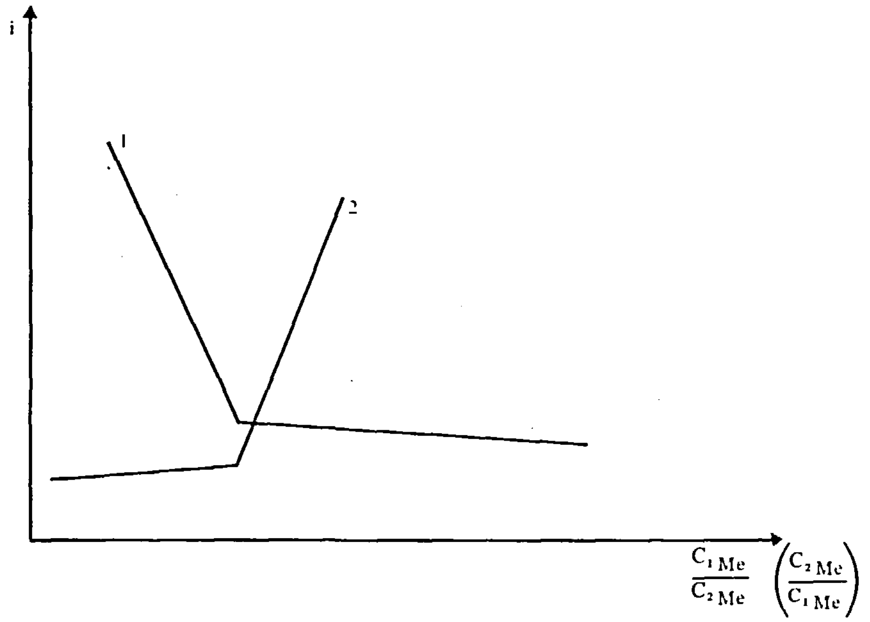

FIGURE 24. Schematic representation of the dependence of the anodic current for the oxidation of one metal from a hanging amalgam electrode on the ratio of concentrations of two metals in the amalgam. For curve 1, the metal yielding the anodic current was present in the amalgam initially; for curve 2, the metal yielding the anodic current was added in various amounts to the other metal intially present in mercury.

intersect at the point where the concentration ratio is equal to the atom ratio of metals in the intermetallic compound. When the stoichiometry of the compound has been found, the solubility product of the compound may be estimated from the current at the point of intersection. It should be remembered, however, that during the polarographic oxidation the concentration of the metal that is oxidized at the amalgam-solution interface is drastically diminished. As a result, the compound tends to dissociate into the simple metals, and if the rate of this dissociation is appreciable, a kind of kinetic current will be observed. In such a case, it may be impossible to obtain reliable information about the intermetallic compound studied. Moreover, the method is rather time-consuming, because several amalgams in quite large quantities have to be prepared, and there is some danger of air-oxidation while they are being prepared, transferred to the polarographic apparatus, and subjected to polarographic examination. For these reasons, this method is only rarely applied to the study of complex amalgams.

4.1.3. Voltammetry at Hanging Mercury-drop Electrodes

This method was developed[197] soon after the HMDE began to find wide applications. It is very simple and fast, although it is almost impossible to obtain precise results of thermodynamic parameters if the reaction between metals in mercury is not sufficiently rapid. However, the composition of the intermetallic compound may be determined with good accuracy.

To study the formation of such compounds a series of solutions should be prepared. These should all contain the same concentration of one metal ion, $_1$Me, but the concentration of the second metal ion, $_2$Me, should increase from zero to values exceeding two or three times the concentration of the first metal ion. These solutions (with added background electrolyte) are electrolyzed at the HMDE, using a potential that is sufficiently negative to reduce both of the metal ions. After this deposition, which must be carried out under exactly the same conditions for each one of the solutions, the behavior of the resulting complex amalgam formed by electrodeposition is examined, usually by anodic single-sweep voltammetry.

If the two metals react in mercury to form an intermetalic compound, the anodic peak current of the metal $_1$Me whose concentration was the same in all of the solutions will decrease as the concentration of $_2$Me increases. This decrease is proportional to the extent of the chemical reaction and the concentration of the second metal.

Typical curves that may be obtained in such an investigation are shown in Figure 25.

The point of intersection of two line segments corresponds to the equivalence point of the reaction between the metals. To find the composi-

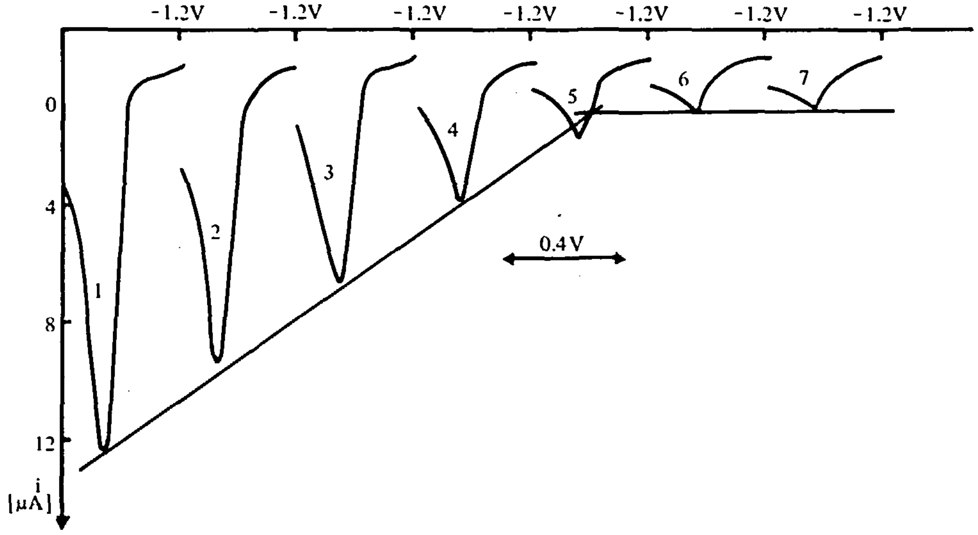

FIGURE 25. Anodic curves for the oxidation of tin from complex tin-nickel amalgams formed in the HMDE. The amalgams were obtained by electrolysis, at -1.2 V for 2 min, of an 0.1 *M* KCl solution containing 2×10^{-4} *M* $ZnSO_4$ and the following concentrations of $NiSO_4$: (1) 0, (2) 5×10^{-5}, (3) 1×10^{-4}, (4) 1.5×10^{-4}, (5) 2×10^{-4}, (6) 2.5×10^{-4}, and (7) 3×10^{-4} *M*.

tion of the compound precisely, the ratio of the cathodic peak currents of the two metal ions must be determined with a solution in which their concentrations are equal, for unless this ratio is equal to 1, the metals will not be deposited in the same proportions as those at which their ions are present in the solutions. The product of this ratio by the ion-concentration ratio at the equivalence point gives the composition of the compound.

The procedure may be further simplified by starting with a solution of one metal ion at a known concentration in the electrolytic cell. To this solution there are added samples containing known amounts of the second metal ion; after each addition, the cathodic deposition of both metals at the HMDE is carried out, followed by the electrooxidation of the resulting amalgam. This procedure resembles the well-known amperometric titration.

It is obvious that the oxidation of amalgams may be carried out under conditions other than described here, as, for example, by using chronopotentiometry or chronoamperometry.

In this method, as in amalgam polarography, decomposition of the intermetallic compound may occur during the oxidation, and if this is extensive, it may influence the correctness of the results.

4.1.4. Controlled-potential Coulometry

Controlled-potential coulometry was first applied to the study of the formation of intermetallic compounds in mercury by Ficker and Meites.[88] Solutions containing known amounts of two ions in a supporting electrolyte are electrolyzed with a mercury cathode of large volume (35 cm^3) at a potential sufficiently negative to effect quantitative deposition. After a suitable period of electrolysis (which in some experiments was as long as 140 hr to ensure that equilibrium had been attained in the formation of the intermetallic compound), the working potential was changed to a value at which the more easily oxidized metal is reoxidized when it is present alone. Measurements of current as a function of electrolysis time were made during the stripping.

This method was used and further developed by Rodgers and Meites[198] to the study of the reaction between nickel and zinc in mercury. The results of their experiments are shown in Figure 26. The current early in the electrolysis is due chiefly to the oxidation of free, uncombined zinc, while that at later times represents the slower oxidation of intermetallic compound.

The quantity of uncombined zinc was determined by subtracting the current corresponding to the oxidation of the intermetallic compound (curve a) from the total current measured experimentally. The resulting curve b corresponds to oxidation of uncombined zinc. The current integral Q_{Zn} associated with this line segment was considered to correspond to the amount of uncombined zinc in the amalgam, and the number Q_C of moles of electrons corresponding to the oxidation of zinc combined with nickel in the intermetallic compound was obtained from

$$Q_C = Q^o_{Zn} - Q_{Zn} \qquad (4.14)$$

where Q^o_{Zn} is the number of moles of electrons corresponding to the entire amount of zinc known to be present.

If the formation of a single intermetallic compound $NiZn_m$ consumed all of the nickel as well as the bound zinc, the value of m could be obtained from the equation

$$m = \frac{Q_C}{Q^o_{Ni}} \qquad (4.15)$$

where Q^o_{Ni} is the number of moles of electrons corresponding to the total amount of nickel present. It was found experimentally that the value of m was equal to 1.0 within experimental error if Q^o_{Zn}/Q^o_{Ni} were between 1.1 and about 2.5. From a series of such experiments, the authors were able to conclude that the compound NiZn is insoluble in mercury and to evaluate its solubility product.

Further details of this method may be found in the original papers.[88,198] It seems that this method should give reliable results and should be widely applied in practice.

4.2. Complex Amalgam Systems Investigated by Electrochemical Methods

Complex amalgams having gold as one of their components have been among the most frequently investigated systems. This brief review of the properties of some complex amalgams will begin with discussions of those systems.

4.2.1. Complex Amalgams Containing Gold

4.2.1.1. The Gold-zinc-mercury System

This system was investigated as long ago as

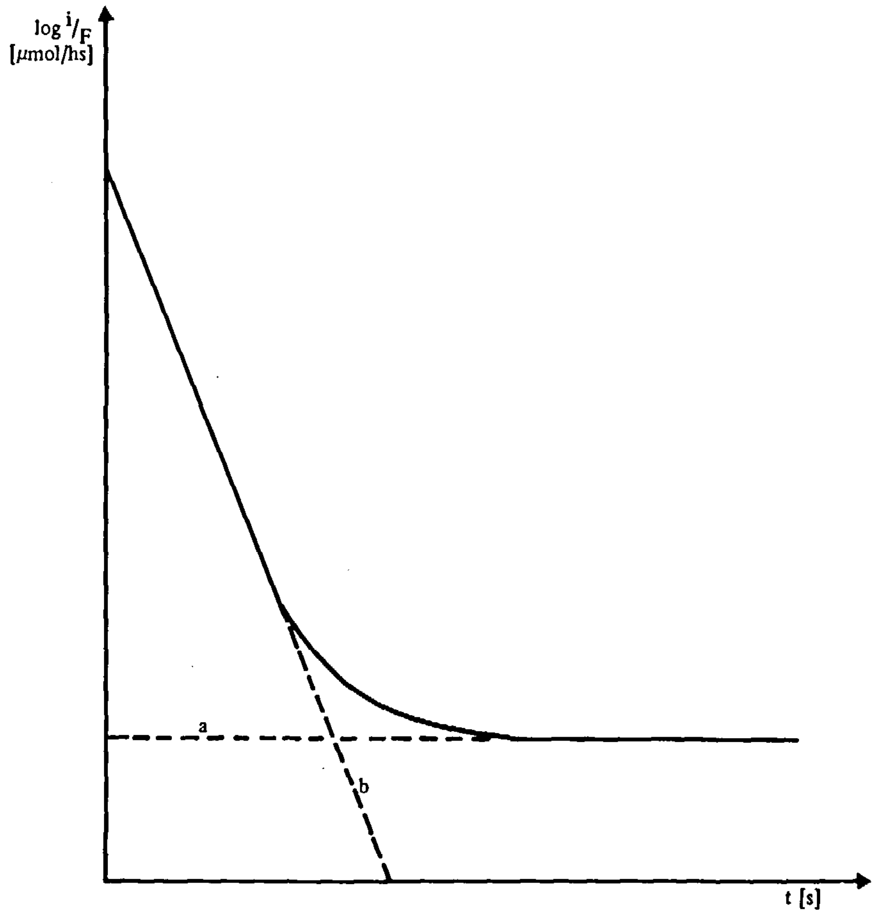

FIGURE 26. Dependence on time of the logarithm of the current for the anodic oxidation of a nickel-zinc amalgam at constant potential. Line a represents the extrapolated current for the oxidation of an intermetallic compound; line b represents the current for the oxidation of uncombined zinc, and is obtained by subtracting the current given by line a from the total current.

1922 by Tammann and Jander,[146] who used the potentiometric method and found that an intermetallic compound is formed.

Hartmann and Schölzel,[194] who also used potentiometry, later studied the equilibrium of this reaction, and found the composition of the compound to be AuZn. Hartmann and Schölzel interpreted their measurements by assuming the compound to be soluble in mercury, and they calculated its stability constant on the basis of that assumption. Kemula and Galus,[199] who studied the kinetics of formation of AuZn by chronopotentiometric reduction on mercury and gold-amalgam electrodes, also assumed that this reaction proceeds in a homogeneous phase.

The results of Hartmann and Schölzel were later reinterpreted by Zebreva,[200] who showed that AuZn exists in mercury as a solid phase. This conclusion was based on calculations of the solubility product of AuZn for various concentrations of gold and zinc in the amalgam. This parameter was nearly constant, whereas the homogeneous stability constant calculated from the same concentrations was not. However, it should be mentioned that the absolute value of K_{so} given by Zebreva[200] is not correct.

Stromberg et al.,[193] using a procedure elaborated by themselves, recalculated the data of Hartmann and Schölzel and obtained $K_{so} = 1 \times 10^{-8}$ at 90°C. Subsequent authors have given values of K_{so} at 25°C: Rodgers and Meites[198] give $(7.1 \pm 0.6) \times 10^{-10}$, and Gumiński and Galus[195] give 5.4×10^{-10}. The experiments performed by these workers led them to conclude, in agreement with Zebreva, that AuZn exists in mercury as a sparingly soluble compound. This conclusion is also supported by data obtained in the potentiostatic deposition of zinc on gold amalgam at potentials at the foot of the reduction wave of zinc(II): the cathodic current drops initially, but then an increase of current is observed. This fact may be interpreted as reflecting the occurrence of crystallization after some induction period.

In other chronocoulometric experiments it was impossible to find any evidence of the formation of soluble, weakly dissociated AuZn, whose formation would precede that of solid AuZn. If the undissociated species does exist, its concentration is apparently too low to be detected by using double-potential-step chronocoulometry with an integration time of the order of 5 ms.

Gumiński and Galus[195] have also studied the temperature dependence of K_{so} and calculated the enthalpy of formation of AuZn. They obtained a value of ΔH that was equal to -17.9 kcal mol^{-1}, which is close to earlier results,[194,201] and found that ΔS changes from 18.8 (at 15°C) to 18.2 cal deg^{-1} mol^{-1} (for 75°C).

4.2.1.2. The Gold-cadmium-mercury System

This system was also investigated by Hartmann and Schölzel,[194] who reported the formation of the intermetallic compound with the formula AuCd. As they did with AuZn, Hartmann and Schölzel assumed that AuCd exists as a soluble compound in the mercury phase, and consequently they calculated its stability constant.

Zebreva reinterpreted their values to show that the compound has only a limited solubility in mercury, but her results are erroneous in respect to absolute values.

Gumiński and Galus[202] found evidence for the crystallization of AuCd in this system. It was obtained from measurements of the rate of the reaction occuring between cadmium and gold, and also from potentiostatic experiments similar to those described above for the gold-zinc-mercury system.

On the basis of potentiometric experiments, Gumiński and Galus calculated the solubility product of AuCd in mercury, using the procedure described in Section 4.1.1. K_{so} was found to be equal to $(2.1 \pm 0.7) \times 10^{-5}$ at 25°C. This solubility product is slightly higher than the one, 1.2×10^{-5}, obtained by recalculating the results of Hartmann and Schölzel. However, the agreement of these two values is sufficiently close to confirm the reliability of the method used by Gumiński and Galus.

Studies[202] mentioned above on the kinetics of formation of AuCd showed that the elaboration of that problem by earlier workers[194] was not correct. Using various initial concentrations of gold and cadmium in the amalgam and assuming that the reaction proceeds by second-order kinetics in a homogeneous system, Gumiński and Galus found the rate constant to vary over no less than four orders of magnitude.

Further work on this problem is needed.

4.2.1.3. The Gold-indium-mercury System

Zebreva and Levitskaya[203] have found two compounds, AuIn and Au_3In, to be formed in this system. Their solubility products were found to be $K_{so\ (AuIn)} = (1.9 \pm 0.7) \times 10^{-6}$ and $K_{so\ (Au_3In)} = 10^{-12}$. The investigation carried out by Mesyats[204] revealed the formation of only one compound, which had the formula AuIn and a solubility product equal to 9×10^{-6}. However, Kozin and Dergacheva,[205] in their potentiometric studies of that system, confirmed the results of Zebreva and Levitskaya regarding the formation of both Au_3In and AuIn.

It has been shown that both of these compounds exist in the solid phase. On the basis of a phase diagram one might expect $AuIn_2$ to be formed as well, but the potentiometric experiments did not reveal the formation of this compound. However, Kozin and Dergacheva obtained values of solubility products that were quite different from those given by Zebreva and Levitskaya: these were $(2.2 \pm 0.6) \times 10^{-5}$ for AuIn and $(4.1 \pm 0.7) \times 10^{-9}$ for Au_3In, both at 16°C. It seems that these values should be regarded as being more precise and reliable than those given earlier. Values of the thermodynamic parameters for the formations of these compounds are given in Table 10.[205]

The kinetics of the interaction of Au and In has also been investigated.[205] The interaction was fast in homogeneous amalgams, but considerably slower when a heterogeneous gold amalgam was used.

The formation of AuIn was found to be faster than that of Au_3In. The transformation of Au_3In into AuIn is slow since it proceeds in the solid phase.

TABLE 10

Thermodynamic Parameters for the Formation of Intermetallic Compounds in the Au-In-Hg System

Compound	$\Delta G°$ (kcal mol^{-1})	$\Delta H°$ (kcal mol^{-1})	$\Delta S°$ (cal deg^{-1} mol^{-1})
Au_3In	-11.0	-8.2	11
AuIn	-5.8	-7.9	7

4.2.1.4. The Gold-tin-mercury System

The formation of an intermetallic compound in the gold-tin-mercury system was reported by Tamman and Ohler,[206] who found heat to be evolved during the dissolution of tin in gold amalgam. Galus[207] later found that the composition of the compound is given by the formula AuSn. However, Kovaleva and Zebreva,[208] using a similar method, described the composition as $AuSn_2$. Kemula and co-workers,[209] in opposition to Kovaleva and Zebreva, reported the formation of AuSn. They found, using amalgam polarography, that AuSn is poorly soluble in mercury and determined its solubility product.

In their second work, Kovaleva and Zebreva[210] arrived at the conclusion that two compounds are formed in this system: both AuSn and the previously postulated $AuSn_2$. Their solubility products were given as $(1.7 \pm 0.4) \times 10^{-6}$ and $(9 \pm 6.5) \times 10^{-10}$, respectively.

Kozin and Dergacheva[211] concluded that solid compound AuSn is formed, and that its calculated solubility product is dependent on the concentration of gold in the amalgam. The solubility product extrapolated to 0 amalgam concentration is equal to 8.9×10^{-7} at 25°C. These authors reported the following thermodynamic parameters for the formation of AuSn: $\Delta G^0 = -8.07$ kcal mol^{-1}, $\Delta H = -9.7$ kcal mol^{-1}, and $\Delta S = -7.5$ cal deg^{-1} mol^{-1}. This value of ΔH is not much different from that given[212] for the formation of AuSn in the gold-tin system.

Kemula and co-workers[209] had also found that the solubility product of AuSn appears to depend on the concentrations of gold and tin in the amalgam. To explain this phenomenon they assumed that dimers of tin, Sn_2, exist in equilibrium with solid AuSn. However, in later potentiometric studies carried out in our laboratory by Dowgird,[167] it was found that the solubility product of AuSn is equal to $(9.0 \pm 1.0) \times 10^{-7}$ and is practicially independent of the amalgam composition. It may be that the solubility products were not precisely determined in the earlier studies because amalgam polarography was used; the current due to the oxidation of tin resulting from the decomposition of AuSn might be significant.

Dowgird showed that AuSn decomposes to an appreciable extent within the duration of a chronoamperometric oxidation, and such a decomposition may also explain why considerably higher solubility products have been obtained when amalgam polarography has been used.

The kinetics of formation of AuSn has also been studied,[213] but the formation of a solid product was not taken into account in the interpretation of the data. In addition, Kozin and Dergacheva, who studied the kinetics of the reactions occurring in the system, applied a technique similar to that used by Hartmann and Schölzel.

A new study of the system from the point of view of crystallization of the intermetallic compound should be carried out in the future.

4.2.1.5. The Gold-manganese-mercury System and Other Complex Amalgams Containing Gold

The gold-manganese-mercury system has been investigated by Galus,[207] who found that an intermetallic compound is formed between gold and manganese and has the composition AuMn.

Further studies of the system were performed by Dowgird,[167] who used potentiometry and hanging amalgam electrodes in her experiments. It is not easy to obtain reproducible results because the reactivities of manganese amalgams are so high. Better reproducibility was found when the concentrations of both gold and manganese in the amalgams were relatively large (about 5×10^{-3} *M*). The formation of a compound having the formula AuMn was confirmed. It was also proved that this compound is only slightly soluble in mercury, and its solubility product was found to be 2.3×10^{-7}. The reaction is quite fast as one may judge from the rate of change of potential after the deposition of manganese into a gold amalgam.

Other complex amalgams containing gold have also been studied in the author's laboratory. The formation of the compound AuCu in the gold-copper-mercury system was found;[214] its solubility product is equal to 5×10^{-6}. There are chemical interactions between gold and nickel[215] and between gold and gallium[215,216] in mercury, but further work on these complex amalgams should be carried out. No interaction of gold with thallium, lead, or bismuth could be detected[215] even by using relatively concentrated (0.05 *M*) gold amalgam.

4.2.2. *The Zinc-nickel-mercury System*

Kemula and Galus have investigated[217] this system by effecting the deposition of zinc and nickel at the HMDE, followed by oxidation of the complex amalgams obtained. They found that the compound NiZn is formed in this system, and ascribed to it the oxidation peak that was observed at −0.1 V vs. S.C.E.

This result was later confirmed by Bukhman and Nosek,[218] who also prepared much larger volumes of the amalgam electrolytically, as well as by Krasnova and Zebreva.[242] Because only small currents were obtained on oxidizing NiZn, Bukhman and Nosek concluded that its solubility in mercury is limited.

An extended study of the system was published by Rodgers and Meites.[198] Using controlled-potential electrolysis, these authors proved that NiZn is only slightly soluble, and they gave its solubility product as $(1.0 \pm 0.3) \times 10^{-8}$. NiZn is formed almost exclusively if the concentration of zinc in excess is small, but if the ratio of the initial concentration of zinc to that of nickel is above about 2.5, another compound, $NiZn_3$, appears. According to Rodgers and Meites, the latter compound is soluble in mercury, and its dissociation constant is given by

$$K = [Ni]\,[Zn]^3/[NiZn_3] = (6.0 \pm 0.7) \times 10^{-10}\ M^3$$

Observations regarding the mechanism of oxidation of zinc from complex zinc-nickel amalgams led them to conclude that NiZn undergoes direct oxidation to nickel(II) and zinc(II).

4.2.3. *The Tin-nickel-mercury System*

In the binary tin-nickel system, the following intermetallic compounds are known: Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4. On investigating complex nickel-tin amalgams prepared by electrodeposition of these metals at the HMDE, Kemula and Galus found[217] that the intermetallic compound NiSn is also formed in mercury. Its formation was shown by the manner in which the anodic current of tin was affected by the presence of nickel in the amalgam.

The formation of NiSn in mercury was later confirmed by Zebreva and Kovaleva,[219] who calculated that its solubility product is equal to 1.4×10^{-12} at 20°C.

Starzewski[220] has made an extensive study of the tin-nickel-mercury system in the writer's laboratory and has confirmed that the deposition of nickel and tin into an HMDE yields the compound NiSn. However, on depositing these metals together with mercury onto a carbon-paste electrode and following the oxidation currents of the resulting amalgams, one finds that the ratio Ni/Sn is in the range from 0.7 to 0.8, close to 0.75. This suggests that the compound Ni_3Sn_4, which is known to exist in the binary nickel-tin system, is formed in the ternary nickel-tin-mercury system as well. The difference between this result and that found with the use of the HMDE may be due to the fact that the diffusion coefficient of nickel in mercury is lower than that of tin in mercury and to the consequent possible crystallization of nickel on Ni_3Sn_4 crystals.

Coulometric oxidations of the excess of tin from larger quantities of complex tin-nickel amalgams of larger quantity have also shown that the atomic ratio Ni/Sn in the compound lies within the range from 0.7 to 0.8.

Using carbon-paste electrodes and changing the concentration of mercury(II) in the solution while keeping the concentrations of tin(II) and nickel(II) constant, one can prepare amalgams having different mercury contents by electrolysis. By oxidizing these amalgams, it was shown that the intermetallic compound does not contain mercury.

From measurements of the e.m.f. of the cell

$$Sn(Hg)|Sn^{2+},\ 1\ M\ HClO_4\ |\ Ni_3Sn_4, NiHg_4, Hg \qquad (4.16)$$

the following thermodynamic parameters for the formation of Ni_3Sn_4 were found: $\Delta G^0 = -54.7$ kcal mol^{-1}, $\Delta H^0 = -79$ kcal mol^{-1}, and $\Delta S^0 \doteq -81$ cal deg^{-1} mol^{-1}.

The kinetics of the formation of the compound in the tin-nickel system has also been investigated by Starzewski. During electrodeposition of tin at constant potential on platinum covered by $NiHg_3$, current peaks typical of electrocrystallization processes were observed. These data cannot be interpreted quantitatively because the distribution of $NiHg_3$ on the electrode was not known precisely.

4.2.4. The Zinc-cobalt-mercury System

This system has been studied by Babkin and Kozlovskii,[221] Ficker and Meites,[88] and Hovsepian and Shain.[222] All these authors found an intermetallic compound to be formed by the interaction of zinc with cobalt and agree that it has the formula CoZn; Ficker and Meites found that several other compounds were present as well. Babkin and Kozlovskii assumed that CoZn is soluble in mercury and found its stability constant to be 120 ± 40 by amalgam polarography and potentiometric measurements.

Ficker and Meites were unable to calculate a solubility product that was acceptably constant, and accordingly concluded that the compound has the formula CoZn but that it exists in equilibrium in mercury with dimers of cobalt and zinc. These views were later supported by Hovsepian and Shain,[222] who used very different techniques and conditions. The agreement is puzzling because these conclusions must be wrong: the solubility of cobalt in mercury is very low, Rodgers and Meites[114] have since shown that zinc amalgams do not contain diatomic Zn_2 at any proportions approaching those required, and Scott and Meites,[241] in a re-examination of the zinc-cobalt-mercury system, have obtained data strongly suggesting that the compound CoZn is only slightly soluble in mercury. Further work on the system is needed.

4.2.5. The Tin-copper-mercury System

This complex amalgam has been investigated by Kovaleva and Zebreva,[223] who reported the formation of two compounds, Cu_3Sn and CuSn, both only slightly soluble in mercury.

According to these authors, their solubilities are quite similar, and their solubility products are: $K_{so\,(CuSn)} = 4.6 \times 10^{-6}$ and $K_{so(Cu_3Sn)} = 2.8 \times 10^{-12}$. There is one intermetallic compound in the system that is soluble in mercury, and its stability constant is equal to 5×10^7.

However, in the same year Zebreva et al. published a new paper[225], which may be considered to be an extension of the earlier studies[223] and which also described the formation of two compounds, CuSn and Cu_3Sn. These conclusions were based on measurements of the potentials of mixed amalgams.

4.2.6. The Copper-antimony-mercury and Cadmium-antimony-mercury Systems

Several intermetallic compounds exist in the binary copper-antimony system. Zebreva and Kozlovskii[8] pointed out that several compounds also may be formed in the cadmium-antimony-mercury system. However, Stromberg et al.[226] found only one compound, CdSb.

In later studies, Zakharchuk and Zebreva,[227] using the deposition of metals at the HMDE, found that CuSb was formed if the ratio [Cu]/[Sb] of the concentrations of the metals in the amalgam was lower than 2 and the time between preparation and oxidation of amalgams was of the order of 2 to 3 min. At longer times Cu_2Sb was formed, and if the ratio of [Cu]/[Sb] in the amalgams exceeded 2, Cu_2Sb was formed regardless of the time for which the amalgams were aged. The solubility product of that compound at 25°C is equal to $(4.3 \pm 0.4) \times 10^{-12}$. If the ratio of concentrations [Cu]/[Sb] in the amalgam is higher than 5, the composition of the compound may be given by the formula $Cu_{3+x}Sb$, with x changing from 1.4 to 2.5.

Zakharchuk et al.[228] have also investigated the interaction of metals in the cadmium-antimony-mercury system by depositing the metals into hanging mercury-drop electrodes. The formation of CdSb was reported, in agreement with earlier results of Zebreva,[229] and its solubility product was found to be $(2.1 \pm 0.3) \times 10^{-8}$.

4.2.7. The Zinc-alkali Metal-mercury and Indium-alkali Metal-mercury Systems

The formation of the compound $ZnNa_2$ in the zinc-sodium-mercury system was reported by Kozlovskii,[230] but this result was not confirmed in later studies.[231]

Korshunov and co-workers[233] investigated the systems Zn-Me-Hg, where Me is the alkali metal, potentiometrically. No formation of compounds was found with lithium, sodium, or cesium, but in the presence of potassium and rubidium the formation of compounds was observed. The change of the potentials with alkali-metal concentration was analyzed, and crystals of the compounds formed were subjected to chemical analysis. The chemical analyses suggested the existence of the compounds $KZn_{10}Hg_{14}$ and $RbZn_{10}Hg_{13}$, but the potentiometric results pointed to lower contents of zinc.

It was hardly possible to give the solubility products of these compounds, but one may state qualitatively that the compound formed with rubidium is more soluble in mercury than that containing potassium.

The low reactivities of these compounds deserve comment. They are only slowly decomposed by the action of dilute acids. Korshunov and Selevin,[233]. on the basis of potentiometric measurements, found the compounds $RbIn_{10}Hg_{11}$ and $CsIn_{10}Hg_{13}$ to be formed in systems containing indium, an alkali metal, and mercury.

4.2.8. *The Zinc-copper-mercury System*

Complex amalgams containing copper and zinc were studied by Zebreva and Kozlovskii,[196] who reported the formation of CuZn in that system. The formation of an intermetallic compound between zinc and copper has also been reported by Kemula and co-workers.[197] Jangg,[234] on the basis of potentiometric measurements, concluded that the compound has the formula CuZn and exists in the mercury phase as a solid.

Kozin[12] also gave potentiometric results for the zinc-copper-mercury system. Using his data, Zebreva[147] concluded that the solid intermetallic compound CuZn is formed in this system and has a solubility product equal to 4×10^{-6}. On dissolution in mercury, this should be completely dissociated into copper and zinc. The solubility product given by Zebreva is two orders of magnitude higher than that reported by Stromberg and Gorodovykh.[235] Their value is $(5 \pm 1) \times 10^{-8}$.

Rudolph,[236] using stationary-mercury-electrode voltammetry, also found CuZn to be formed and to be sparingly soluble in mercury.

4.2.9. *Other Systems*

Some other complex amalgams also have been investigated electrochemically.

The formation of compounds between silver and zinc and silver and cadmium in mercury was shown qualitatively by Kemula and co-workers.[197] Zebreva[240] found these compounds to have the compositions AgZn and AgCd and gave their solubility products.

Levitskaya and Zebreva[174] have studied the indium-antimony-mercury system. The formation of InSb, for which the solubility product is equal to $(2.2 \pm 0.4) \times 10^{-8}$ at 20°C, has been found.

In some other complex amalgams, interaction between the metals has not been found to occur. For instance, Kovaleva and Zebreva[208] have found that there is no interaction between silver and tin in complex amalgams containing silver at concentrations below 0.05 *M*. Silver and indium also do not react in mercury.[175]

Further work on intermetallic compound formation in complex amalgams should be carried out. The results of such investigations are important in analytical practice.

More information about the properties of such compounds may help in arriving at a better understanding of the nature of such interactions. From that point of view, it would be important to investigate complex amalgams containing an alkali metal or alkaline earth metal.

Complex amalgams with rare-earth metals should also be investigated. Intermetallic compounds are known to form in such systems (see, for instance, Reference 180), but so far they have not been much investigated by electrochemical methods.

GENERAL CONCLUSIONS

It has not been the writer's intention to give a comprehensive review, and there has accordingly been no mention, for example, of the conductivities of amalgams, which are briefly reviewed in the book of Belashchenko.[237]

In recent years the natures of the intermetallic compounds formed in mercury have been much discussed. Some workers consider that such compounds may exist only as solids, whereas others[238] assume that both compounds that are insoluble and compounds that are soluble in the mercury phase may be formed. There is some evidence in this review that the second view is more realistic.

It may be that, in the case of the compound formed between gold and tin in mercury, there is a soluble but only partially dissociated compound present in the mercury and in equilibrium with the solid phase. This view may be supported by the fact that there is a significant difference between the solubility products as determined by potentiometry and amalgam polarography.[209] The much higher result obtained by the latter technique may be attributable to the existence, and decomposition during the anodic oxidation, of the compound that is dissolved in mercury.

It should be pointed out that the formation of AuSn has also been detected spectrophotometrically in mixtures of the vapors of these two metals,[183] and also that there is an order in liquid AuSn, at temperatures slightly exceeding its melting point, which is similar to that in solid AuSn.[239]

Similar behavior has also been reported for some other systems and may be found for complex liquid amalgams, especially when the difference between the electronegativities of the dissolved metals is large.

It is difficult to decide whether, in simple amalgams (for instance, those of sodium or potassium), there exist intermetallic compounds with constant compositions or, alternatively, whether the dissolved metals are solvated by mercury with different heats of solvation. It seems that both views may be correct. If compounds having definite compositions are formed, they are probably also solvated, and the extent of this outer-sphere solvation by mercury atoms may be largely dependent on the ratio of concentrations of dissolved metal and mercury. Hence, it seems that the calculations of Zebreva and co-workers[126] do not suffice to reject the concept of the formation of compounds having definite compositions between the alkali metals and mercury. It should also be mentioned that the very high solvation numbers given by them are not clear from the point of view of a model of such a solvate.

These and many other problems should be attacked in the future. The kinetics of formation of intermetallic compounds in mercury should be studied. Almost all of the published results dealing with this problem are most likely more or less incorrect, and electrochemical methods would seem to be well-suited to studies in this area.

More attention should also be paid in the future to amalgams containing the rare-earth metals and to the intermetallic compounds that these metals form with other metals.

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