A REVERSIBLE DROPPING GALLIUM AMALGAM ELECTRODE

DISSERTATION

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By

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PREFACE

Although many investigations of the electrochemistry of gallium have been made since the element's discovery in 1875, a survey of the literature had indicated that few studies had been made of its polarography at the dropping mercury electrode - and these consistently indicated a high degree of irreversibility for the reduction. Further, there was no report that a dropping gallium amalgam electrode had been used to obtain either the anodic or the composite polarographic wave.

It was the initial purpose of this study, therefore, to re-examine the general polarography of gallium especially with reference to the possible fabrication and use of a dropping gallium amalgam electrode.

After the dropping amalgam electrode had been developed, it was decided to extend the study to the polarography of gallium in the presence of thiocyanate in hopes that a reversible wave would be found in this complexing medium.

The polarography of indium was briefly studied as a comparison.

Finally, it is hoped that the results of this investigation may serve as a basis for an extension of the study to include the effect of other complexing anions and contribute to the development of electroanalytical procedures for the determination of gallium.

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In addition, I wish to express my appreciation to The Ohio State University for its assistance in the form of a research fellowship and particularly to the Department of Chemistry for providing generous aid in the form of teaching assistantships.

To my wife, Harriett,
for her patience and
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CHAPTER I

INTRODUCTION

The chemistry of the metal gallium is less familiar in many respects than other elements of the periodic table. Certain of its physical properties are anomalous and, hence, quite interesting. It seems proper, therefore, to begin the discussion of this research with a brief summary of gallium chemistry, followed in turn by a detailed historical account of the electrochemistry of this unfamiliar element.

Gallium: discovery and general chemistry.--^{1,2,3}

(1) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, N. Y., 1953, Chap. 30.

(2) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans Green Co., N. Y., 1922.

(3) C. A. Hampel, "Rare Metals Handbook," Reinhold Publishing Corp., N. Y., 1954, p. 157.

The existence of the element gallium was predicted by both Mendeleeff,⁴ who called it eka-aluminum, and by

(4) D. I. Mendeleeff, Compt. Rend., 81, 969 (1875);
J. Russ. Phys. Chem. Soc., 1, 60 (1869).

Lecoque de Boisbaudran⁵ who postulated its existence from

(5) L. de Boisbaudran, Ann. Chim. et phys., 10, 100 (1877); Chem. News, 35, 148, 157, 167 (1877).

the positions of several anomalous spectral lines. In 1875 de Boisbaudran⁵ reported the actual separation of a small quantity of the element. Its physical properties were found to be very close to those predicted by Mendeleeff. The new element was named after the country in which it was discovered - Gaul (France). Gallium is distributed widely,^{3,6} although in very small amounts (never

(6) E. Einecke, "Das Gallium," Leipzig, Verlag von Leopold Voss, 1937.

more than 0.01% in any material) over the whole of the earth's crust. It occurs in greatest concentration associated with the ores of aluminum, zinc and germanium.

Pure, solid gallium is silvery white in appearance, and, on melting at 29.75°C., is very similar to liquid mercury. Gallium has a strong tendency to wet materials such as glass. Its very great alloying ability^{7,8} causes

(7) Atomic Energy Commission, "Liquid Metals Handbook," Washington Govt. Printing Office, 1950.

(8) W. D. Wilkinson, "Properties of Gallium," ANL-4109, Argonne Nat'l. Lab. 1948.

it to corrode most metals with which it comes in contact. The liquid metal is much less noble than mercury, being attacked slowly by cold mineral acids. However, it passivates easily in contact with cold nitric acid. Gallium is unusual in that it has a very long liquid range: 29.75° to 1983°C . at atmospheric pressure. In relation to its physical properties, especially its low melting point, its position in subgroup IIIB of the periodic table is distinctly anomalous.

The aqueous chemistry of gallium, however, is quite similar to that of aluminum and indium. The trivalent oxidation state is the only one known to be stable in aqueous solutions. There has been some recent indication, however,^{9,10} that lower oxidation states can exist in the

(9) A. W. Davidson and F. Jirik, J. Am. Chem. Soc., 72, 1700 (1950).

(10) A. W. Laubengayer and F. B. Schirmer, ibid., 62, 1578 (1940).

solid gallium chlorides. The sulfide, Ga_2S_3 , cannot be precipitated as such, but it may be obtained as a co-precipitate with zinc sulfide or cuprous sulfide from alkaline solution.

Gallium hydroxide is distinctly amphoteric. The hydroxide is a weaker base than aluminum hydroxide, and is easily dissolved in an excess of alkali with the formation of soluble gallates. The strongly acid character of the trivalent gallium ion causes its soluble salts, e.g., NO_3^- , Cl^- , SO_4^{2-} , ClO_4^- , to be extensively hydrolyzed in aqueous solution. Stock solutions of gallium salts low in gallium concentration may actually become turbid after a few days standing.^{11,12}

(11) T. Moeller and G. King, J. Phys. Colloid Chem., 54, 999 (1950); J. Am. Chem. Soc., 74, 1355 (1952).

(12) G. Challenger, Ph.D. dissertation, Harvard University, 1945.

Gallium may be detected qualitatively¹³ by precipita-

(13) P. E. Browning and L. E. Porter, Am. J. Sci., 44, 22 (1917).

tion with strongly acid potassium ferrocyanide. It may also be determined qualitatively or estimated quantitatively¹⁴ through identification and measurement of its

(14) L. W. Strock, Am. Inst. Mining Met. Engrs., Tech. pub. No. 1866 (1945). Published in Metals Technol., April 1945.

strong spectral line at $2943.6\overset{0}{\text{\AA}}$. Gallium is accurately determined¹⁵ by precipitating its gelatinous hydrous

(15) G. E. F. Lundell and J. I. Hoffman, J. Research NBS. 15, 409 (1935).

oxide, washing and igniting to the sesquioxide, Ga_2O_3 . The dissolved metal may be determined gravimetrically,¹³ or potentiometrically¹⁶ with potassium ferrocyanide or

(16) J. D. Kirschman and J. B. Ramsey, J. Am. Chem. Soc., 50, 1632 (1928).

by a fluorescence reaction after precipitation at pH 2.6 with 8-hydroxyquinoline and subsequent treatment with chloroform.¹⁷ In the past, however, aqueous gallium

(17) E. B. Sandell, Ind. Eng. Chem. Anal. Ed. 13, 844 (1941).

solutions have not lent themselves well to the usual electroanalytical techniques: e.g., polarography, potentiometry, amperometric titration, coulometry or controlled potential deposition.

Electrochemistry of Gallium - historical survey.---¹⁸

(18) H. Fogg, Trans. Electrochem. Soc., 66, 107 (1934).

During the period immediately following the isolation of gallium by de Boisbaudran in 1875, there were many attempts to characterize its electrochemistry, both from a theoretical viewpoint and a practical one, since the electrochemical approach seemed at the time to offer an efficient way to concentrate and separate the scarcely occurring metal. Special attention was placed on its separation from indium and zinc, the elements with which it commonly occurs. This type of separation proved especially difficult to achieve with any efficiency. A survey of these early efforts in the light of modern theory of electrode reactions indicates that under the conditions imposed by these early experiments, the gallium couple exhibited an unusually high degree of irreversibility.

The first reported attempt to electrolyze gallium⁵ was made by its discoverer, L. de Boisbaudran, who achieved some measure of success in separating gallium from strong alkaline solutions. His early efforts were soon supplemented with work reported by Schucht,¹⁹

(19) L. Schucht, Chem. Ztg., 4, 292 (1880).

Ehrlich,²⁰ Kunnert²¹ and Uhler²² who also reported the

(20) L. Ehrlich, ibid., 9, 78 (1885).

(21) G. Kunnert, ibid., 9, 1826 (1885).

(22) H. S. Uhler and P. E. Browning, Am. J. Sci., 42, 389-98 (1916).

negative effect of nitrate ion on the electrolysis of gallium from alkaline solutions. In this same period, J. Regnauld²³ attempted to determine an electrode

(23) J. Regnauld, Compt. rend., 86, 577 (1878).

potential for the gallium couple. In 1904, Thiel²⁴ and

(24) A. Thiel, Ber., 37, 175 (1904).

in 1907 Mathers²⁵ studied the possibility of separating

(25) F. C. Mathers, J. Am. Chem. Soc., 29, 485 (1907).

indium and gallium by electrolysis.

Later Dennis and Bridgman²⁶ in a study of the chemistry

(26) L. M. Dennis and J. A. Bridgman, J. Am. Chem. Soc., 40, 1531 (1918).

of gallium attempted to separate the metal from indium by electrolysis. Their work confirmed earlier reports which had indicated the slowness of the metal reduction process from strong alkaline hydroxide. At the current densities used in their work they found that high concentrations

of K^+ and Na^+ were a distinct disadvantage. Dennis and Bridgman appear to have been the first to attempt, with any success, the separation of indium and gallium from a sulfuric acid solution. After repeated electrolysis at high current densities, they were able to find no spectral lines for indium in the resulting solution.

Richards and Boyer²⁷ repeated the Dennis and Bridg-

(27) T. W. Richards and S. Boyer, J. Am. Chem. Soc., 41, 133 (1919).

man work and found that gallium could be deposited at low acid concentrations, while indium separated out at high concentrations of sulfuric acid. Both separations were very dependent on the current density.

These same authors²⁷ attempted, in 1931, to determine the standard potential of liquid and solid gallium electrodes. Measurements were made on solutions of "neutral" gallium sulfate. For a 1.0 N solution of the gallium salt they found the reduction potential to be approximately -0.25 volt, vs. N.H.E., a value which they attributed to a very pronounced negative drift in potential. The free energy of transition from solid to liquid which they calculated did not agree with that calculated using J. Regnauld's²³ value for the standard potential. Although the authors recognized that extensive hydrolysis existed

in their solutions, they made no correction for it.

The work of S. Von Bergkampf,²⁸ in 1932, appears to

(28) S. Von Bergkampf, Z. Elektrochem., 38, 847 (1932).

have been the first attempt to obtain a valid standard oxidation potential. His value of +0.52 volt vs. N.H.E. was obtained after correcting for activity using the activity coefficients reported by Lewis and Randall²⁹

(29) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 378.

for La^{+3} .

About this time Reichel³⁰ attempted the quantitative

(30) E. Reichel, Z. Anal. Chem., 87, 321 (1933).

separation of gallium electrolytically. He plated gallium onto platinum from ammonium sulfate solutions, but obtained variable results.

The first comprehensive study of the electrochemistry of gallium was the work of Otto Stelling,³¹ who published,

(31) O. Stelling, Z. Elektrochem., 41, 712-21 (1935); 41, 779-89 (1935).

in 1935, two papers dealing with the subject. The first was concerned with determining a standard potential for the gallium couple. His efforts to obtain reproducible null-point (i.e., zero current) potentials in gallium chloride solutions using either liquid gallium or solid gallium electrodes were unsuccessful, although he noted that the liquid gallium electrode came to equilibrium very quickly, in spite of the fact that it exhibited considerable passivity.

In an attempt to lessen the difficulties associated with using the pure liquid gallium metal, Stelling prepared a gallium amalgam electrode. Only a few studies³²⁻³⁵

(32) W. Ramsay, J. Chem. Soc., 55, 533 (1889).

(33) Davies and Keeping, Philos. Mag., I, 145 (1929).

(34) N. A. Puschin, S. Stepanovic and V. Stajic, Z. Anorg. Chem., 209, 330 (1932).

(35) E. S. Gilfillan and H. E. Bent, J. Am. Chem. Soc., 56, 1663 (1934).

had been made on the solubility of gallium in mercury at room temperature prior to Stelling's work, and only one investigation³⁶ has since been reported.

(36) W. M. Spicer and H. W. Bartholomay, J. Am. Chem. Soc., 73, 868-9 (1951).

The Ga-Hg alloys were prepared in Stelling's study by passing liquid gallium through a capillary into the mercury. The capillary was used to strip the liquid gallium of surface oxide and adhering scum. The entire operation was performed in an atmosphere of hydrogen. The coat of oxide which appeared after several hours was reported not to have affected the results.

Stelling reported that the Ga(Hg) (pool) electrode came to equilibrium slowly with the gallium chloride solution, and finally exhibited a potential of -0.887 to -0.888 volt vs. Normal Calomel Electrode (N.C.E.). In 0.1 molar sodium gallate which was also 0.36 normal in sodium hydroxide, the electrode showed -1.512 volt vs. N.C.E. This potential was observed to change markedly with pH.

In order to improve his results Stelling fabricated a dropping gallium amalgam electrode. The concentrations of the amalgams reported ranged from 0.25% to 0.05% gallium by weight.

With the dropping gallium amalgam electrode Stelling obtained E_{null} values for eight concentrations of gallium chloride which ranged from 5.7×10^{-5} to 7.7×10^{-3} molar (hydrolysis was minimized by the addition of hydrochloric acid). The potentials which he obtained, corrected for activity using the activity coefficients of La^{+3} reported

By Lewis and Randall,³⁷ varied randomly from -0.909 to

(37) Lewis and Randall, Loc. cit.

-0.902 volt vs. N.C.E. He concluded on the basis of the reproducibility of the measured potentials that the system behaved in a reversible manner. Using Stelling's results, Einecke⁶ calculated $E^{\circ}_{\text{Ga},\text{Ga}^{+3}}$ to be +0.56 volt vs. N.H.E.

In a subsequent study of gallium polarization curves on both solid and liquid gallium as well as on mercury and platinum, Stelling³¹ noted that the liquid gallium was more noble than the solid in its electrode reactions. In fact, his study of the temperature dependence of the electrode potential showed a well-defined break at the melting point.

Using a liquid gallium electrode dropping from a small glass tube having a large orifice and controlled at the top by a rubber bulb, Challenger,¹² in 1945 reported a reproducible standard oxidation potential of +0.57(8) volt versus the normal hydrogen electrode (N.H. E.) (at 25°C.) for the solid metal. He obtained this value after correcting the potential of the liquid gallium for the heat of transition to the solid state.

In 1953 Saltman and Nachtrieb³⁸ made a thermodynamic

(38) W. Saltman and N. Nachtrieb, J. Electrochem. Soc., 100, 126-30 (1953).

study of cells of the type

where X was Cl^- or ClO_4^- .⁴ Their work confirmed Stelling's findings on the passivity of liquid gallium and in addition showed that solid gallium exhibited potentiometrically reversible behavior. By using the hydrolysis constants obtained from a study made by the Office of Naval Research³⁹ they corrected their oxidation potentials and

(39) Office of Naval Research, Contract 6N-ori-71, Chemistry Task XVII, University of Illinois, Bimonthly Report, No. 5.

obtained, after extrapolation to infinite dilution, a value of +0.560 volt vs. N.H.E. at 25°C. Their study also yielded a series of activity coefficients for gallium chloride at ionic strengths that ranged from 0.10 to 0.35 molar.

Polarography of gallium.--The first reported investigation of the polarography of gallium appears to have been made by S. Takagi,⁴⁰ who in 1928 studied its polarographic

(40) S. Takagi, J. Chem. Soc., London, 301 (1928).

reduction in sulfate media. He was, however, unable to obtain a reduction wave for this ion.

S. Zeltzer⁴¹ made a study of gallium polarography

(41) S. Zeltzer, Coll. Czech. Chem. Comm., 4, 319 (1934).

and reported a reduction wave which occurred at $E_{1/2} = -1.1$ volts vs. saturated calomel electrode (S.C.E.) in a solution containing no more than 10^{-3} molar hydrochloric acid. In a more acidified solution the wave became coincident with that of hydrogen. He also reported the presence of a wave in $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$, but Challenger,¹² some years later, was unable to confirm the behavior in ammoniacal solution.

Challenger found a single, well-developed polarographic wave for the reduction: $\text{Ga}^{+3} + 3\text{e} = \text{Ga}^0$, in dilute potassium chloride having the "natural" pH of hydrolysis. A second hydrolysis wave at $E_{1/2} = -1.5$ volts vs. S.C.E. was also noted in this solution. In 0.1 molar potassium chloride containing 0.005% gelatin, he found that $E_{1/2}$ for gallium reduction shifted from -1.03 to -1.15 volts vs. S.C.E. when the concentration of Ga^{+3} was increased from 0.1 to 5.0 millimolar. A plot of E_{applied} vs.

$\log \frac{i_d - i}{i}$ in 0.1 molar potassium chloride showed a

straight line which gave a reciprocal slope of 0.083 volt compared with the theoretical reciprocal slope of 0.020 volt indicated by the Heyrovsky-Ilkovic equation for a

reversible 3 electron reduction.

Challenger, and later Zittel,⁴² suggested that this

(42) H. Zittel, Ph. D. dissertation, Vanderbilt: Diss. Abstr., 14, 1303 (1954).

excessive slope may indicate a disproportionation of Ga^{+2} to the metal. A reversible reduction of Ga^{+3} to the metal would have an $E_{1/2}$ near -0.81 volt vs. S.C.E.

In 1953 DeSesa and co-workers⁴³ sought, unsuccess-

(43) M. A. DeSesa, D. N. Hume, A. C. Glamm and D. D. DeFord, Anal. Chem., 25, 983 (1953).

fully, to electroreduce gallium from a buffer solution containing 2.0 molar each of acetic acid and ammonium acetate.

Zittel's work⁴² has confirmed the polarographic findings of Challenger, and in addition has shown that the limiting current of the Ga^{+3} reduction wave is pH-dependent and reaches a maximum value at $\frac{(\text{H}^+)}{(\text{Ga}^{+3})} = 50$. He concluded that gelatin was a most effective agent for suppressing the cathodic Ga^{+3} maximum. There was no mention, however, of finding an hydrolysis wave.

P. A. Giguere and D. Lamontagne⁴⁴ and recently

(44) P. A. Giguere and D. Lamontagne, Science, 120, 390 (1954).

Grahame⁴⁵ have reported an investigation of a dropping

(45) D. Grahame, Anal. Chem., 30, 1736 (1958).

gallium metal electrode. The former workers observed drop times that were very erratic, and they were troubled by an oxide coating on the liquid gallium. A current-voltage curve which they⁴⁴ obtained in an air saturated 0.1 molar potassium chloride solution indicated that the potential of the dropping gallium electrode, at zero current, was -1.0 volt vs. S.C.E.

Vinogradova and Chudinova⁴⁶ have extensively studied

(46) E. N. Vinogradova and N. N. Chudinova, Zavodskaya Lab., 22, 1280 (1956); C.A., 51, 11131b (1957).

the polarography of gallium in numerous supporting electrolytes. They found that gallium cannot be polarographically determined in perchlorate, nitrate, chloride, sulfate, acetate, citrate sulfosalicylate or Trilon (EDTA). This conclusion conflicted in the case of nitrate and chloride, with the results obtained by both Zittel and Challenger which have already been described. These Russian authors state, however, that Ga^{+3} may be determined in solutions of either sodium thiocyanate, potassium thiocyanate or ammonium thiocyanate buffered with salicylic

acid at a pH of 2.8 to 3.4, provided ethanol is added to suppress the maximum.

During the next year, 1957, a second Russian group^{47,48} reported finding a well-developed polarographic

(47) A. I. Zelyanskaya and N. V. Bausova, Zhur. Fiz. Khim., 31, 440 (1957); C.A., 51, 15309C (1957).

(48) A. I. Zelyanskaya and N. V. Bausova, Izvest. Vostochn. Filial, #7, 51-3 (1957); 52, 9844 (1958).

wave for gallium in a solution 0.1 molar in both sodium salicylate and sodium chloride having a pH of 2.5 to 4.5. An $E_{1/2}$ value of -0.988 volt vs. S.C.E. was observed, and the existence of the complex species $Ga(C_6H_4O_2COO)_3^{-3}$ was postulated.

These investigations are significant, because, for the first time, an anion system had been found which made a noticeable improvement in the polarographic behavior of gallium. It would appear on comparing the two investigations that the constituent responsible for the enhanced character of the wave, and which was common to both test solutions, was salicylate ion. Vinogradova and Chudinova did not report, however, the effect of thiocyanate per se on the reversibility of gallium reduction.

Micka,⁴⁹ reporting in 1956, found that the best

(49) K. Micka, Coll. Czech. Chem. Comm., 21, 862-5 (1956).

developed polarographic waves were obtained in ammoniacal solutions.

Polarography of indium.--J. Heyrovsky⁵⁰ is considered

(50) J. Heyrovsky, Chem. Listy, 19, 168 (1925).

the first to have studied the reduction of indium at the dropping mercury electrode. Takagi,⁴⁰ in a study several years later, found that the indium wave was "reversible" in 0.1 molar potassium chloride and exhibited a deposition potential of -0.500 volt vs. N.C.E. He found also that the deposition potential depended on the chloride concentration and was shifted to more negative (more reducing) potentials as the chloride concentration increased.

Takagi⁴⁰ also noticed that the presence of sulfates adversely affected the reduction wave. This behavior he attributed to the possible formation of basic indium sulfates. As part of a general investigation of the equation of Heyrovsky and Ilkovic,⁵¹ Tomeš⁵² concluded that indium

(51) J. Heyrovsky and D. Ilkovic, Coll. Czech. Chem. Comm., 7, 198 (1935).

(52) J. Tomeš, Coll. Czech. Chem. Comm., 9, 12 (1937).

reduction showed reversible behavior in a solution which was 1.0 molar in potassium chloride and found the wave to have a half-wave potential of -0.635 volt vs. N.C.E.

Lingane⁵³ observed that indium is irreversibly

(53) J. J. Lingane, Ph. D. dissertation, University of Minnesota, 1938; J. Am. Chem. Soc., 61, 2099 (1939).

reduced from perchloric acid solutions. A drawn-out wave having a pronounced maximum was observed which had an $E_{1/2}$ value of -0.95 volt vs. S.C.E. He found that the maximum could be suppressed by the addition of small amounts of methyl red or gelatin. Upon adding chloride or iodide to the solution the wave improved in shape and moved to more positive (less reducing) potentials, indicating the possible formation of halide complexes.

Lingane reports an $E_{1/2}$ value of -0.561 volt and -0.597 volt vs. S.C.E. in 0.1 molar and 1.0 molar potassium chloride respectively. The latter potential appears to agree with that obtained by Tomes⁵² in the same electrolyte. Lingane's investigation confirmed Takagi's⁴⁰ report that sulfate suppressed the diffusion current, and also showed that a very peculiar "minimum" occurs in the diffusion current plateau of the indium wave in 1.0 molar potassium chloride which he found could be eliminated upon the addition of methyl red.

Schufle, Stubbs and Witman⁵⁴ in their polarographic

(54) J. A. Schufle, M. F. Stubbs and K. E. Witman, J. Am. Chem. Soc., 73, 1013 (1951).

study of the chloride complexes of indium reported a reversible polarographic wave for the reduction of 0.001 normal indium perchlorate in 0.1 normal perchloric acid. They state that a plot of E_{applied} vs. $\log(\frac{1}{i_d - i})$ gave a straight line having nearly theoretical slope and indicated a half-wave potential -0.573 volt vs. S.C.E. This seems unusual, since the potential (-0.561 volt) reported by Lingane in 0.1 molar potassium chloride is 12.0 millivolts more positive.

The comprehensive investigation of indium polarography reported by Bulovova⁵⁵ confirmed Lingane's observa-

(55) M. Bulovova, Coll. Czech. Chem. Comm., 19, 1123 (1954).

tion of an irreversible indium wave in perchlorate solution. Bulovova also noted a well-defined wave in potassium nitrate containing 0.01% gelatin to suppress the maximum and a very sharply defined wave in thiocyanate media. It was also reported in Bulovova's work that an indium amalgam, dropping into a 0.5 molar potassium chloride containing a dissolved indium salt, showed a reversible,

composite wave.

In 1956 Greiner and Meites⁵⁶ reported finding

(56) J. W. Greiner and L. Meites, Anal. Chim. Acta, 14, 482-94 (1956).

polarographic waves for indium in solutions which were 1.0 and 10.0 molar in thiocyanate. The waves were fairly well defined but exhibited the minimum on the diffusion current plateau first noted by Lingane.⁵³

Nakatani⁵⁷ studied indium polarography in formic and

(57) H. Nakatani, J. Sci. Hiroshima Univ., Ser. A. 20, 49-54 (1956).

acetic acids.

Aksel'rud and Spivakovskii⁵⁸ have determined indium

(58) N. V. Aksel'rud and V. B. Spivakovskii, Zhur. Anal. Khim., 12, 78-82 (1957).

in solutions containing potassium bromide, and Aksel'rud⁵⁹

(59) N. V. Aksel'rud, Ukrain. Khim. Zhur., 31, 457 (1955).

has shown that indium complexes (co-ordination number of 4) with $\text{SO}_4^{=}$.

The historical description of the important developments in the electrochemistry of gallium, as presented here, represents a complete survey of the literature to this time. It is significant in this coverage to note the paucity of work that has been done in the field of gallium polarography. Gallium appears to be one of the few elements of the periodic table whose electrochemistry remains to be well defined.

The description of indium polarography as outlined here is not intended to be definitive. Several aspects of gallium electrochemistry which were met in studying this problem suggested that a brief comparison of the results with those obtained for indium was advisable. This brief historical survey of indium polarography then serves as a basis for that comparison.

STATEMENT OF THE PROBLEM

It was evident from a survey of the literature that the irreversibility of the gallium couple, as exemplified by the unusual difficulty encountered in its electro-deposition from aqueous solutions, has been a real reason contributing to the unavailability of this unusual metal and thus indirectly to the scarcity of knowledge concerning its chemistry.

From the electrochemical point of view the irreversibility of the gallium couple is significant because of its magnitude, which is anomalously large for its physical properties and its position in subgroup IIb of the periodic table.

This investigation was thus directed toward a general clarification of gallium electrochemistry with its irreversibility as the primary concern.

The polarographic method appeared to be a powerful tool for this type of study. Since dropping amalgam electrodes are considered most useful for studying the criteria of reversibility, and, because no evidence existed to indicate that the dropping gallium amalgam electrode had been used previously to obtain polarographic waves, the problem thus resolved itself into the following principal parts:

1. An investigation for the first time of the preparation and possible use of a dropping gallium amalgam electrode

to obtain polarographic waves.

2. An evaluation and comparison of the general polarographic behavior of gallium with that of indium in thiocyanate solutions.

CHAPTER II

ELECTROCHEMICAL THEORY

Because this problem is concerned with a study of polarographic reversibility, it seems appropriate at this time to discuss briefly several fundamental ideas concerning the subject of galvanic cells and electrochemical reversibility. ^{60,61,62}

(60) G. Khortum and J. O. M. Bockris, "Electrochemistry," Elsevier Publishing Co., N. Y., 1951.

(61) S. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand, Inc., N. Y., Chap. VIII, 1952.

(62) J. A. V. Butler, "Electrocapillarity," Chemical Publishing Co., Inc., 1940.

Galvanic cells.--In its simplest form a galvanic cell may consist of two dissimilar electrodes immersed in a solution of an electrolyte or two similar electrodes immersed in the same electrolyte at different concentrations. The latter type is usually referred to as a concentration cell.

The potential of a galvanic cell is the algebraic sum of essentially three separate interface potentials⁶⁰:

(a) metal-metal junction; (b) metal-solution interface; (c) solution-solution interface. The potential of a galvanic cell may be so defined that the value measured can be attributed to the algebraic sum of only the two

metal-solution interface potentials. The equilibrium (that is, null-point or zero current) potential observed, then, is characteristic of the total chemical reaction which is capable of occurring across the two electrodes.

When such a galvanic cell is shorted externally through a metallic conductor, a current will flow whose relation to the quantity of chemical reaction causing it has been given by Faraday.⁶³

(63) M. Faraday, "Experimental Researches in Electricity, 1831-1838," London, 1839.

Reversibility.--Klotz⁶⁴ has stated that, "For thermodynamic purposes one way of viewing a reversible process

(64) I. M. Klotz, "Chemical Thermodynamics," Prentice-Hall Inc., N. Y., 1950, p. 33.

is as a succession of thermodynamic states, each of which is in a condition of equilibrium. For such a situation an infinitesimal change in external conditions will cause a reversal in the succession of states which make up the process."

It is generally known that the operation of galvanic cells may, under certain conditions, approach the reversibility described by Klotz. When a potentiometer is connected to the terminals of such a cell, the reactions

occurring at each electrode may be completely reversed by the imposition of an e.m.f., which is larger by an infinitely small amount than the equilibrium potential of the cell itself.

Ideally,⁶⁵ a reaction may not proceed a finite

(65) E. C. Potter, "Electrochemistry, Principles and Applications," Cleaver-Hume Press, Ltd., London, 1956.

amount in any direction in a truly reversible manner. In the case of a "reversible" galvanic cell, however, a very small current may actually flow without changing the equilibrium potential of the cell by an amount large enough to be measured. Within the limits of experimental measurement, therefore, the cell appears to be operating reversibly. In subsequent discussions concerning reversibility this latter, operational definition will be implied unless otherwise specified.

A galvanic cell is operating irreversibly, then, when the current flow is of sufficient magnitude to displace, sensibly, the cell potential from its equilibrium value.⁶¹ The cell in this condition is said to be polarized.

Polarography.--Although Kucera⁶⁶ appears to have been

(66) G. Kucera, Ann. Physik, 11, 529 (1903).

the first to work with dropping mercury electrodes (D.M.E.), Jaroslav Heyrovsky⁶⁷ coined the word

(67) J. Heyrovsky, Chem. Listy, 16, 256 (1922).

polarography to mean the determination and measurement of current-voltage (C-V) curves with the dropping mercury electrode. The polarographic method of analysis was devised by Heyrovsky at the Charles University, Prague, Czechoslovakia, and reported in the literature in 1922.

In 1925 Heyrovsky and Shikata⁶⁸ invented an instru-

(68) J. Heyrovsky and M. Shikata, Rec. trav. chim., 44, 496 (1925).

ment which they called the Polarograph, to record automatically current-voltage curves at the dropping mercury electrode. The name polarograph was subsequently copyrighted by these two authors. A more general designation for this method of analysis is the term voltammetry, so-called by Kolthoff and Laitinen⁶⁹ because it is more

(69) I. M. Kolthoff and H. A. Laitinen, Science, 92, 152 (1940).

descriptive of electrochemical processes occurring at a microelectrode.

The polarographic method of analysis consists usually in applying a voltage across a cell composed of an unpolarizable electrode (the reference electrode) and a polarizable dropping mercury microelectrode - the working electrode. The dropping mercury electrode assumes the applied potential, since the electrode potential of the unpolarizable electrode is not appreciably altered during the flow of small currents (microamperes).

When the dropping mercury electrode is placed in a polarographic cell containing an electroactive substance and the potential varied in a continuous fashion, a certain value of the applied potential will be reached at which the dissolved species will begin to oxidize or reduce. Current will begin to flow in the external circuit at an increasing rate until the rate of the electrode reaction equals the rate at which the reacting species is supplied to the electrode surface by the sum of diffusion, convection and migration (barring a kinetically controlled reaction). A further increase in applied potential causes the current to increase at a decreasing rate. A limiting value of the current is finally reached which is proportional under certain conditions to the bulk concentration of the reacting substance.

Since several excellent descriptions^{70,71,72} of

(70) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, N. Y., 1952.

(71) L. Meites, "Polarographic Techniques," Interscience Publishers, N. Y., 1955.

(72) G. W. C. Milner, "The Principles and Applications of Polarography," Longmans Green Co., 1957.

polarographic theory and practice already exist, this discussion will be limited to a detailed examination of that aspect of fundamental polarographic theory which directly concerns the problem.

The Ilkovic equation.--The fundamental equation which describes the behavior of the current at the dropping mercury electrode when mass transfer to the drop surface is controlled entirely by diffusion was originally derived by D. Ilkovic⁷³ and later in a more rigorous manner

(73) D. Ilkovic, Coll. Czech. Chem. Comm., 6, 498 (1934).

by MacGillavry and Rideal.⁷⁴ The equation,

(74) D. MacGillavry and I. K. Rideal, Rec. trav. chim., 56, 1013 (1937).

$$(1) \quad i_t = 0.732 n F_y D^{1/2} C m_{2/3} t^{1/6},$$

describes the behavior of the polarographic current at any time, t , over the life of the mercury drop.

The equation which describes the average current (i.e., the "integrated" form of equation (1)), which is the one most often used in polarographic analysis is

$$(2) \quad i_{ave.} = 607 n D^{1/2} C m^{2/3} t_{max.}^{1/6},$$

where

i = current in microamperes averaged over the life of the drop. (amperes $\times 10^{-6}$)

607 = a constant which includes the value of the Faraday, F (96500 coulombs)

n = number of Faradays of electricity involved in the reaction

D = diffusion coefficient of the reacting species
($\frac{cm^2}{sec}$)

C = concentration of the reacting substance
($\frac{moles \times 1000}{liter}$)

m = mass of mercury which flows from the capillary in 1 second ($\frac{mg}{sec}$)

t = time necessary for the formation of one drop (seconds)

It has been shown by Lingane and Loveridge,⁷⁵

(75) J. J. Lingane and B. A. Loveridge, J. Am. Chem. Soc., 72, 438 (1950).

Strehlow and Von Stackelberg⁷⁶ and Kambara and Tachi⁷⁷

(76) H. Strehlow and M. Von Stackelberg, Z. Electrochem., 54, 51 (1950).

(77) T. Kambara and I. Tachi, "Proceedings International Polarographic Congress," Prague, Feb. 1951, p. 126.

that the original derivation of the Ilkovic equation did not account for the curvature of the mercury drop. Their equation

$$(3) \quad i_{ave.} = 607 n D^{1/2} C m^{2/3} t^{1/6} \left(1 + \frac{AD^{1/2} t^{1/6}}{m^{1/3}} \right)$$

differs from equation (2) only in the correction term,

$$\left(1 + \frac{AD^{1/2} t^{1/6}}{m^{1/3}} \right).$$

The constant, A, is given by Lingane

and Kambara et al. as 39. Strehlow and Von Stackelberg, however, report a value of 17. The correction term in the brackets has a value of about 1.1 for most substances, when a value of 39 is substituted for A.

Dependence of the diffusion current on temperature.-- If the Ilkovic equation as described in equation (2) is rewritten⁷⁸ - that is,

(78) D. Ilkovic, Coll. Czech. Chem. Comm., 10, 249 (1938).

$$(4) \quad i_{d_{ave.}} = k n D^{1/2} C m^{2/3} t^{1/6}, \text{ so that}$$

the "constant," 607, i.e., $607 = \left(\frac{3455}{d_{Hg}^{2/3}} \right)$ is recognized

as being temperature dependent - every term except n is temperature dependent. By taking the natural logarithm of both sides of equation (4) and differentiating with respect to the absolute temperature, T , the temperature coefficient of the diffusion current⁷⁹ is obtained:

(79) Kolthoff and Lingane, op. cit. p. 92.

$$(5) \quad \frac{1}{i_d} \cdot \frac{d i_d}{dT} = \frac{1}{k} \cdot \frac{dk}{dT} + \frac{1}{2D} \cdot \frac{dD}{dT} + \frac{1}{C} \cdot \frac{dC}{dT} + \frac{2}{3m} \cdot \frac{dm}{dT} + \frac{1}{6T} \cdot \frac{dT}{dT}.$$

Combining these various coefficients yields

$$(6) \quad \frac{1}{i_d} \cdot \frac{d i_d}{dT} = 0.0037 + \frac{1}{2\lambda^0} \cdot \frac{d\lambda^0}{dT}, \text{ where } \lambda^0 \text{ is the limiting}$$

equivalent ionic conductance.

Equation (6) predicts a coefficient of 1.3 to 1.6 per cent/degree which is in fair agreement with the results of Nejedly,⁸⁰ who found a value 1.3 to 2.3 per cent/degree

(80) V. Nejedly, Coll. Czech. Chem. Comm., 1, 319 (1929).

and also with the work of Von Stackelberg et al.⁸¹

(81) M. Von Stackelberg, P. Klinger, W. Koch and E. Krath, Forschunger Tech. Mitt. Krupp., 2, 59 (1939).

Effect of (m) and (t) on diffusion current.--It can be seen from equation (2) that the diffusion current, i_d , is a linear function of the two-thirds power of the mass of mercury flowing per second and the one-sixth power of the drop time in seconds. That these quantities are significant in the interpretation of the polarographic data has been shown by the work of Lippmann⁸² and of

(82) G. Lippmann, Pogg. Ann., 149, 547 (1873); Ann. chim. phys., 5, 494 (1876); Wiedemann's Ann., 11, 316 (1880).

Kolthoff and Lingane.⁸³

(83) I. M. Kolthoff and J. J. Lingane, J. Am. Chem. Soc., 61, 825 (1939).

Frumkin⁸⁴ and also Grahame⁸⁵ have reviewed the

(84) A. Frumkin, Ergeb. exakt. Naturw., 7, 235 (1928).

(85) D. C. Grahame, Chem. Rev., 41, 441 (1947).

electrical characteristics of mercury-solution interfaces, and J. A. V. Butler has written extensively on the subject.⁶²

The interfacial tension of a mercury-solution interface is a function of the potential impressed on the

mercury and of the composition of the electrolyte. Kolthoff and Lingane⁸³ have noted that when an increasingly negative potential is applied to a mercury electrode dropping into 0.1 molar potassium chloride solution, m varies through a shallow minimum while t , which is a linear function of the interfacial tension, passes through a steep maximum near -0.52 volt vs. S.C.E. and describes a curve very closely resembling the electrocapillary curve for mercury.

The product, $m^{2/3}t^{1/6}$, does not vary sharply with variation in applied potential, however, owing to the fact that it is varying as the sixth power. Near the extreme negative end of the potential scale it decreases more strongly, and the consequent decrease of i_d with decrease in $m^{2/3}t^{1/6}$ must be taken into account in accurate measurements.

The diffusion current constant, first defined by Lingane,⁸⁶ $I = \frac{i_d}{C_m^{2/3}t^{1/6}}$, facilitates the comparison

(86) J. J. Lingane, J. Am. Chem. Soc., 61, 2099 (1939).

of diffusion currents obtained with capillaries having different characteristics.

Effect of complex formation and solvent viscosity on the diffusion current.--J. J. Lingane⁸⁷ has shown that

(87) J. J. Lingane, Ind. Eng. Chem. Anal. Ed., 15, 589 (1943).

ion size as determined by complex formation has a significant effect on the magnitude of the diffusion current in different electrolytes. Tartrate complexes of reducible cations, for example, are more voluminous than their aquo complexes and yield smaller diffusion currents, chiefly because of their smaller diffusion coefficient.

Brasher and Jones⁸⁸ found that diffusion currents

(88) M. Brasher and F. R. Jones, Trans. Faraday Soc., 42, 775 (1946).

of several metals were inversely proportional to the square root of the viscosity (7) of concentrated solutions of sulfuric acid, sodium hydroxide and sodium sulfate. This was confirmed by Lingane and Carritt⁸⁹ who worked with

(89) I. M. Kolthoff and J. J. Lingane, "Polarography," p. 97.

strong solutions of sulfuric acid. This effect has also been studied by the addition of non-electrolytes (e.g., sucrose) to aqueous solutions of electroactive material.⁹⁰⁻⁹²

(90) H. A. McKenzie, J. Council Ind. Research, Australia, 21, 210 (1948).

(91) I. Vavruch, Coll. Czech. Chem. Comm., 12, 429 (1947).

(92) G. Matsuyama, Ph.D. dissertation, University of Minnesota, 1948.

Heyrovsky-Ilkovic Equation and the polarographic half-wave potential (uncomplexed metal ions).--Although free cations do not exist as such in aqueous solution but as the aquo complexes, $M(H_2O)_x^{n+}$, for the purpose of calculation, however, the "free" ion may be assumed to exist.

The derivation of the Heyrovsky-Ilkovic equation given in this discussion is based on the series of equations first reported by Heyrovsky and Ilkovic⁵⁰ and later by Lingane,⁸⁶ and concerns the general processes involved for the reversible oxidation or reduction of a substance from one stable oxidation state to the other.

Given the following fast, reversible equilibrium which is occurring at the surface of the mercury drop:

the Nernst equation⁹³ states that the average potential

(93) W. Nernst, Z. phys. Chem., 4, 129 (1889).

of the drop will vary according to,

$$(8) \quad E_{d.E.} = E_a^{\circ} - \frac{RT}{nF_y} \ln \frac{C_a^{\circ} f_a}{a_{Hg} \cdot C_s^{\circ} f_s}, \text{ where } R, T, n$$

and F_y have their usual significance; C_a° is the concentration of the surface amalgam, a_{Hg} is the activity of mercury, C_s° is the surface concentration of the reducible species, and f_a, f_s are the respective activity coefficients. E_a° is the standard potential of the amalgam vs. the reference cell used - often the saturated calomel electrode (S.C.E.). Equation (8) may then be written

$$(9) \quad E_{d.E.} = (E_a^{\circ} + RT/nF_y \ln a_{Hg}) - RT/nF_y \ln \frac{C_a^{\circ} f_a}{C_s^{\circ} f_s}.$$

In this discussion it will be assumed (a) that the unstirred solution contains an excess of indifferent salt to carry the migration current, i.e., electroactive ions reach the electrode surface entirely by diffusion and (b) that when the concentration of reduced substance at the electrode surface is zero, then

$$(10) \quad C_a^{\circ} = k' i = \frac{i}{k_{red}}, \text{ where } i \text{ is the current with its}$$

appropriate sign, and, from equation (2), $k_{red} = 607 n D^{1/2} m^{2/3} t^{1/6}$; D being the diffusion coefficient for the metal dissolved in the amalgam.

If, initially, the concentration of the reduced form, C_a° , is not zero but is equal to C_a , then the total

concentration of C_a^0 at the electrode surface will be

$$(11) \quad C_a^0 = C_a + \frac{i}{k_{\text{red}}}$$

The same reasoning shows that for the oxidized form (simple metal ion),

$$(12) \quad C_s^0 = C_s + \frac{i}{k_{\text{ox.}}}$$

where $k_{\text{ox.}}$ has meaning similar to $k_{\text{red.}}$.

Assuming that the rate of diffusion, and, hence, the current, is proportional to the difference in concentration of reacting substance between the bulk of the solution and the drop surface and between the interior of the drop and the drop surface, the following general equations hold:

$$(13) \quad i = k_m(C_m - C_m^0).$$

When the applied potential is of sufficient magnitude to completely polarize the electrode, $i = i_d$ (i_d may be either the anodic or cathodic diffusion current); then

$$(14) \quad i_d = k_m C_m, \text{ and } C_m = \frac{i_d}{k_m};$$

where m represents either the metal concentration in the amalgam or the ion concentration in solution.

Using equation (14), and making the proper substitutions into equations (11) and (12), equations describing the surface concentrations of oxidized and reduced forms are obtained:

$$(15) \quad C_a^o = \frac{i_{d_a}}{k_{red}} + \frac{i}{k_{red}} = \frac{-(i_d)_a + i}{k_{red}}$$

$$(16) \quad C_s^o = \frac{i_{d_c}}{k_{ox}} + \frac{-i}{k_{ox}} = \frac{(i_d)_c - i}{k_{ox}}$$

Substituting equations (15) and (16) into equation (9),

$$(17) \quad E_{dE} = E_a^o + \frac{RT}{nF_y} \ln a_{Hg} - \frac{RT}{nF_y} \ln \frac{1-i_{d_a}}{i_{d_c}-i} \frac{f_a k_{ox}}{f_s k_{red}};$$

and rearranging,

$$(18) \quad E_{dE} = E_a^o + \frac{RT}{nF_y} \ln a_{Hg} - \frac{RT}{nF_y} \ln \frac{f_a k_{ox}}{f_s k_{red}} -$$

$$\frac{RT}{nF_y} \ln \frac{1-i_{d_a}}{i_{d_c}-i}$$

From equation (2),

$$(19) \quad \frac{k_{ox}}{k_{red}} = \frac{D^{1/2}_m}{D^{1/2}_m(Hg)}, \text{ then}$$

$$(20a) \quad E_{d.E.} = E_a^o + \frac{RT}{nF_y} \ln a_{Hg} - \frac{RT}{nF_y} \ln \frac{f_a}{f_s} \frac{D^{1/2}_m}{D^{1/2}_m(Hg)} -$$

$$\frac{RT}{nF_y} \ln \frac{1-i_{d_a}}{i_{d_c}-i}, \text{ or}$$

$$(20b) \quad E_{d.E.} = E_{1/2} - \frac{RT}{nF_y} \ln \frac{1-i_{d_a}}{i_{d_c}-i}$$

Equation (20), although derived for the oxidation and reduction of a metal at its dropping amalgam electrode,

is general for the oxidation-reduction of two soluble oxidation states of a metal ion at the D.M.E., or for the simple reduction of a metal ion soluble in mercury in which case equation (20b) becomes, with $i_{d_a}=0$,

$$(21) \quad E_{d.E.} = E_{1/2} = \frac{RT}{nF_y} \ln \frac{i}{i_{d_c}-i}$$

Significance of the $E_{1/2}$.--The first derivative of equation (20), i.e.,

$$(22) \quad \frac{dE}{di} = \frac{RT}{nF_y} \frac{1}{i_{d_c}-i} + \frac{1}{i-i_{d_a}}$$

shows that the slope of the polarographic wave, $\frac{di}{dE}$, is proportional to the concentration of reacting substance and to the number of electrons, n , involved in the reaction.

The wave described by equation (20) is symmetrical about a point located halfway between i_{d_a} and i_{d_c} , that is, at $i = \frac{i_{d_a} + i_{d_c}}{2}$. The potential corresponding to

this point, $E_{1/2}$, is given in the following equation:

$$(23) \quad E_{1/2} = E_a^0 + \frac{RT}{nF_y} \ln a_{Hg} - \frac{RT}{nF_y} \frac{f_a D^{1/2} m^{+n}}{f_s D^{1/2} m(Hg)}$$

Von Stackelberg⁹⁴ and Lingane⁸⁶ have shown how $E_{1/2}$

(94) M. Von Stackelberg, Z. Elektrochem., 45, 466 (1939).

is related to the standard potential. Equation (23) may be expressed in terms of the standard potential of the solid metal instead of that of the amalgam.

Considering the cell,

Lingane and Von Stackelberg have shown that its potential, E_s , is given by

$$(24) \quad E_s = E_a^0 - E_m^0 - \frac{RT}{nF_y} \ln \frac{a_{\text{sat'd.}}}{a'_{\text{Hg}}}, \text{ where } E_m^0 \text{ is}$$

the standard potential of the pure metal measured against the reference electrode. The term $a_{\text{sat'd.}}$ is the activity of the metal in the saturated, two phase amalgam, and a'_{Hg} is the activity of the mercury in the same amalgam.

Substituting the concentration of the amalgam, $C_a \text{ sat'd.}$, in equation (24) yields, upon rearranging,

$$(25) \quad E_a^0 = E_m^0 + E_s + \frac{RT}{nF_y} \ln (C_a f_a)_{\text{sat'd.}} - \frac{RT}{nF_y} \ln a'_{\text{Hg}}$$

Combining equations (20) and (25) gives

$$(26) \quad E_{1/2} = E_m^0 + E_s + \frac{RT}{nF_y} \ln (C_a f_a)_{\text{sat'd.}} \\ - \frac{RT}{nF_y} \ln \frac{f_a D^{1/2}_{m+n}}{f_s D^{1/2}_{m(\text{Hg})}} + \frac{RT}{nF_y} \ln \frac{a_{\text{Hg}}}{a'_{\text{Hg}}}$$

Equation (26) may be approximated to yield,

$$(27) \quad E_{1/2} = E_m^0 + E_s + \frac{.0591}{n} \log (C_a f_a)_{\text{sat'd.}}, \text{ at } 25^\circ\text{C.}$$

Kolthoff and Lingane⁹⁵ have calculated half-wave

(95) Kolthoff and Lingane op cit., p. 198.

potentials from equation (27) for Tl^+ , Zn^{++} , Pb^{++} and Cd^{++} which agree closely with experimentally obtained values.

Temperature coefficient of $E_{1/2}$.--The temperature coefficient of the half-wave potential is very small. A differentiation of equation (27) indicates a theoretical value of

$$(28) \quad \frac{dE_{1/2}}{dT} \quad 25^{\circ}C. = -0.7 \text{ millivolt/degree}$$

showing that a more negative (i.e., more reducing) value should be found for the $E_{1/2}$ at higher temperatures.

Effect of complexing on $E_{1/2}$.--When a "free" metal ion is in equilibrium with one of its complex ions, its concentration will be determined by the position of the equilibrium, i.e., its dissociation constant.

Heyrovsky and Ilkovic,⁵⁰ Von Stackelberg and Freyhold⁹⁶ and J. J. Lingane⁹⁷ have shown, that upon consider-

(96) M. Von Stackelberg and H. Von Freyhold,
Z. Elektrochem., 45, 120 (1940).

(97) J. J. Lingane, Chem. Rev., 29 (1941).

ing the rapidly attained equilibrium,

where M is the metal and X the ligand of charge $-b$, $E_{1/2}$ may be written,

$$(30) \quad E_{1/2} = E_a^0 + \frac{RT}{nF_y} \ln a_{\text{Hg}} + \frac{RT}{nF_y} \ln \frac{K_c f_{\text{mx}} k_a}{f_a k_c} - p \frac{RT}{nF_y} \ln C_x f_x$$

where,

$$K_c = \text{dissociation constant} = \frac{C_m^0 (C_x^0)^p f_x^p f_m}{C_{\text{mx}}^0 f_{\text{mx}}} \quad \begin{array}{l} \text{electrode} \\ \text{surface} \end{array}$$

f_{mx} = activity coefficient of the complex

f_x = activity coefficient of the ligand

p = coordination number of the complex.

It may be seen, then, that the $E_{1/2}$ "simple" will be moved to more negative values for small K_c 's and increasing ligand concentrations.

Equation (30) may be used as such for determining the "coordination number", p , of the complex ion. A more convenient method of obtaining accurate values for p and for the formal dissociation constant k_c' may be used if the expression for the $E_{1/2}$ value of the simple, uncomplexed ion is subtracted from equation (30) to yield,

$$(31) \quad E_{1/2} = (E_{1/2_c} - E_{1/2_s}) - \frac{RT}{nF_y} \ln \frac{K_c f_c k_s}{f_s k_c} - p \frac{RT}{nF_y} \ln C_x f_x.$$

A plot of $E_{1/2}$ vs. $\ln C_x f_x$ would yield $p RT/nF_y$ as the slope, and $K_c \left(\frac{f_c k_s}{f_s k_c} \right)$ as the intercept if $\text{antiln} (E_{1/2})$

is plotted vs. C_X and extrapolated to $C_X=0$.

DeFord and Hume⁹⁸ have devised equations using (31)

(98) D. D. DeFord and D. Hume, J. Am. Chem. Soc.,
73, 5321 (1951).

which permit the determination of P_1 and K_{c1} for a system containing i complexes in equilibrium.

Ringbom and Eriksson⁹⁹ have extended the ideas

(99) A. Ringbom and L. Eriksson, Acta Chim. Scand.,
7, 1105 (1953).

developed by Lingane and DeFord and Hume by describing a method for determining consecutive complexity constants even though the electrode reaction in question is irreversible.

Polarographic maxima and the isoelectric point of mercury.--Since the problem of this investigation, as previously described did not involve a study of the theoretical aspects of polarographic maxima, no attempt will be made to describe the extant theories concerning these as yet unresolved phenomena.^{100,101,102,103}

(100) J. Heyrovsky, Actualities Scientifiques et industrielles No. 90, Paris, 1934.

(101) D. Ilkovic, Coll. Czech. Chem. Comm., 8, 13 (1936).

(102) H. J. Antweiler, Z. Elektrochem., 43, 596 (1937); 44, 719, 831, 888 (1938).

(103) M. Von Stackelberg, H. J. Antweiler, and L. Kieselbach, ibid., 44, 663 (1938).

Empirically, however, it is well known that maxima - anomalous peaks of current on cathodic (anodic) polarographic waves - are essentially of two kinds: (1) positive when they occur on the positive side of the isoelectric point of mercury (i.e., -0.56 volt vs. N.C.E. or (2) negative when they occur on the negative side, that is when the mercury drop is negatively charged with respect to the solution. Noncapillary-active anions will often reduce or eliminate the former kind and noncapillary-active cations the latter. The same selectivity as to charge seems to hold, in general, for capillary-active ions. Capillary-active nonelectrolytes, for example gelatin or Triton X-100 (a commercial wetting agent) are effective over a rather wide potential range.

Because of the unusual effect of thiocyanate ion on the polarography of gallium, which will be discussed later, it seems proper at this point to mention that Heyrovsky and Vascutzanu¹⁰⁴ have shown that $(SCN)^-$ has a

(104) J. Heyrovsky and E. Vascutzanu, Coll. Czech. Chem. Comm., 3, 418 (1931).

very great effect in shifting the isoelectric point of mercury to more negative potentials. Frumkin¹⁰⁵ has given

(105) A. Frumkin, Ergeb. exkat. Naturw., 1, 254 (1928).

the effect of various anions on the isoelectric point of mercury:

Table 1

Effect of 1.0 N Solutions of Anions
on Isoelectric Point of Mercury

Anion	E (volts vs. N.C.E.) Isoelectric
ClO_4^-	-0.55
Cl^-	-0.56
NO_3^-	-0.56
Br^-	-0.65
SCN^-	-0.72
I^-	-0.82
$\text{S}^=$	-0.92

It can be seen from Table 1 that ClO_4^- and NO_3^- have little or no effect on the isoelectric point of mercury.

Criteria for polarographic reversibility.--Fundamental bases for the existence of thermodynamic

reversibility, as discussed previously, require that the system remain at equilibrium and that any change must take place in infinite time. These criteria are too stringent to be met in actual practice. Several good, theoretical discussions^{60,62,65,106,107} of electrochemical reactions

(106) S. Galsstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co. Inc., N. Y., 1941.

(107) J. O. M. Bockris, "Modern Aspects of Electrochemistry," Butterworth Scientific Publications, London, 1954.

at electrode surfaces have indicated that a net current flow across a metal-solution interface is the result of a difference of two rate processes, one for the oxidation process and the other for the reduction process. If equilibrium is restored to the system by applying a potential of opposite sign, both rates will become equal, and no net transfer of charge will occur.

When the electrochemical equilibrium is displaced slightly, the resulting current flow (flux) will be the difference between the forward and backward rates ("exchange" currents) which may be either large or small in absolute magnitude. If the exchange currents are large, so that the net flux is the small difference between large quantities, it will require the imposition of

only a small change in potential to restore the system to equilibrium. But if the opposite is true, i.e., the exchange currents are small in absolute magnitude, then a larger potential change will be necessary to restore equilibrium.

Conversely, if an electrode system having large exchange currents maintains its equilibrium potential within the limits of experimental error when a small current is flowing, it is said to be "reversible". The same current would cause a different electrode, having smaller exchange currents, to change from its equilibrium potential, thus causing it to behave irreversibly.

The Heyrovsky-Ilkovic equation (equation 20), previously derived, is based on the strict thermodynamic precepts first described by W. Nernst,⁹³ and it represents a limiting equation for all polarographic reactions. For a reaction to be polarographically reversible it must obey the Heyrovsky-Ilkovic equation; the reaction must attain its equilibrium potential during the life of a single drop (usually 2 - 4 seconds).

Equation (20) may be written in the condensed form,

$$(32) \quad E_{d.E.} = E_{1/2} - \frac{0.0591}{n} \log \frac{i - i_{d_a}}{i_{d_c} - i} \quad \text{at } 25^{\circ}\text{C.}$$

The principal experimental criteria for polarographic reversibility according to equation (32) are the following:

- (a) A plot of $E_{D.E.}$ vs. $\log \frac{i - i_{d_a}}{i_{d_c} - i}$ should yield a

straight line.

(b) The slope of the straight line obtained in (a) must have the theoretical slope, $\frac{0.0591}{n}$ volt, at 25°C.

(c) $E_{1/2}$ must be independent of the concentration of reactants (see equation 20).

(d) Anodic, composite and cathodic half-wave potentials must be equal.

(e) A further, necessary criterion is that the polarographic current of a composite wave should show no inflection as it crosses the axis of zero current.

Experimental verification of polarographic reversibility requires, then, an observation of the anodic, composite and cathodic behavior of the substance in question. For reactions of the type, $M = M^{+n} + ne$, anodic and composite waves require the use of a dropping amalgam electrode, whereas the cathodic waves may be obtained in the usual way with the dropping mercury electrode.

Since a study of the reversibility of the gallium electrode was a main topic of interest in this investigation and because no indication could be found in the literature that a dropping gallium amalgam electrode had been used in polarographic work, construction of such an electrode was undertaken. It is fitting, therefore, to present at this time a brief description of polarography using the dropping amalgam electrode.

Dropping amalgam electrodes.--When a metal is soluble in mercury its amalgam may be used as a dropping electrode in a manner similar to that which is used for the dropping mercury electrode.

Lingane¹⁰⁸ first reported a well-defined anodic wave

(108) J. J. Lingane, J. Am. Chem. Soc., 61, 976 (1939).

for the dropping cadmium amalgam electrode (which was 0.01% by wt. in cadmium) and Heyrovsky and Kalousek¹⁰⁹ reported,

(109) J. Heyrovsky and M. Kalousek, Coll. Czech. Chem. Comm., 11, 464 (1939).

about the same time, a theoretical and experimental study of the dropping amalgam electrodes of copper, lead, cadmium and zinc which they had begun several years previous. They derive a relationship similar to that of equation (20) and state that the $E_{1/2}$ occurs when

$$i = \frac{i_d^a + i_d^c}{2} .$$

M. Von Stackelberg and H. Von Freyhold⁹⁶ investigated dropping amalgam electrodes, and in 1950 Strehlow and Stackelberg⁷⁶ reported an approximation for the original Ilkovic equation which they said described the behavior of the current at dropping amalgam electrodes.

$$(33) \quad i = 607 \, n \, D^{1/2} \, C \, m^{2/3} \, t^{1/6} \left[1 - \frac{28.5 \, D^{1/2} \, t^{1/6}}{m^{1/3}} \right]$$

They found, too, that the $E_{1/2}$ potential for the anodic wave obtained with the dropping amalgam electrode varied somewhat with the mass of the amalgam flowing per second.

The work of Turner and Winkler¹¹⁰ agrees qualitative-

(110) R. C. Turner and C. A. Winkler, Can. J. Chem., 29, 469 (1951).

ly with that of Strehlow and Stackelberg, and in addition they found that, for a lead amalgam and flow rates in excess of 1.2 mg/second, a linear relationship between $\frac{i_{da}}{C_a}$ and M occurred. No such relationship, however, was

found for a cadmium amalgam.

Furman and Cooper¹¹¹⁻¹¹² have made an excellent

(111) N. H. Furman and W. C. Cooper, J. Am. Chem. Soc., 72, 5667 (1950).

(112) N. H. Furman and W. C. Cooper, ibid., 74, 6183 (1952).

detailed study of the amalgam polarography of lead, zinc, cadmium, copper, thallium,¹¹¹ and in addition have discussed the subject of metal diffusion coefficients in

mercury.¹¹² Cooper¹¹³ extended these studies and reported

(113) W. C. Cooper, J. Am. Chem. Soc., 77, 2074 (1955).

the results of a comprehensive investigation of the dropping tin amalgam electrode.

As just described, the historical summary relates nearly all the available work which has been done on amalgam polarography since its inception in 1939. Raboul and Bon,¹¹⁴ however, have studied oscillographic current-

(114) G. Raboul and F. Bon, Compt. rend., 224, 1263 (1947).

time curves for dropping amalgam electrodes and were able to obtaine some useful information relating to the diffusion of metals in mercury. Heyrovsky and Forejt¹¹⁵ studied

(115) J. Heyrovsky and Forejt, Z. Physik. Chem., 193, 77 (1943).

potential-time curves, using an impressed alternating current voltage of 50 cycles, for dropping amalgams of copper, bismuth, lead, thallium and cadmium at amalgam concentrations of 0.003% by weight.

CHAPTER III

EXPERIMENTAL MEASUREMENTS

Electrical measurements.--The electrical measurements which were made during the course of this investigation were essentially of three main types: (1) potentiometric, (2) conductometric and (3) polarographic.

Potentiometric.--Potential measurements were often made of dry cells and storage batteries, and on occasion it was necessary to check potential differences in the circuits during the construction and operation of the electrical apparatus. In these instances a commercial vacuum tube voltmeter was used (R.C.A. "Voltohmyst" type 195A.)

Null point measurements of the potential of galvanic cells or of the IR drop across a specific resistance were made using a Leeds and Northrup model K-1 potentiometer (Leeds and Northrup Co., Philadelphia, Pa.) which was a part of the manually constructed polarographic circuit to be described later.

Conductometric.--Conductance-resistance measurements were made with an alternating current (1000 cycles/second) multi-range conductivity bridge, model RCl-B, manufactured by the Industrial Instruments Co., Inc. This bridge was used to measure the electrolytic resistance of polarographic cells and to determine accurately the values of wire wound resistors used as standards.

On the latter occasion the conductivity bridge was calibrated using a Leeds Northrup 10,000-ohm standard resistor (Catalog number 4040). The balance point indicator on this type bridge is of the "magic eye" variety and allows a very precise resistance measurement.

Polarographic.--Two types of polarographic measurements were made: qualitative and quantitative.

Qualitative data were obtained using the Electrochemograph (Catalog number 62200), an automatic recording instrument for obtaining voltammetric data, manufactured by the Leeds Northrup Co., Philadelphia. The principle of operation and the electrical circuit of this instrument are described in detail in the catalog furnished by the manufacturer.

Although the automatic instrument can be used for accurate measurements after a suitable calibration procedure, quantitative data in this investigation were obtained manually with an instrument constructed by the author especially for this purpose.

General descriptions of several good, manual polarographic circuits^{116,117,118} are to be found in the

(116) Kolthoff and Lingane op. cit., Chapt. XVI.

(117) Milner loc. cit.

(118) Meites loc. cit.

literature. It was desired to have available in this

investigation an instrument which could measure potentials accurately (to ± 0.0001 volt) and reproducibly, and whose circuit would be capable of measuring accurately either cathodic or anodic currents.

The essential circuit for such an instrument had already been devised by Professor J. I. Watters¹¹⁹ of

(119) J. I. Watters, Rev. of Sci. Instruments, 22
851-53 (1951).

this department. The significant characteristic of this circuit is in the fact that the applied potentials are taken from a bridge of calibrated, fixed resistors, that is, once the bridge has reached temperature equilibrium it will always deliver the same potential to the polarographic cell.

Two modifications were made of the Watters' circuit:

(1) A second potential dividing bridge was substituted for the rheostat immediately following the battery power supply, for it was found that when potentials were taken from the first divider and applied across the calibrated resistance bridge, potentials delivered to the polarographic cell tended to be more reproducible and more accurately adjustable than otherwise. (2) The circuit was further modified by adding a circuit for calibration of the external galvanometer.

Figure 1 shows the detailed circuitry of the complete polarographic bridge and galvanometer calibration circuit.

The individual components as labeled in Figure 1 are defined according to the following:

- A: 17 contact, single section wafer switch
- B: 100 ohm WW center contact radio type potentiometer
- C: 1.0 ohm WW center contact radio type potentiometer
- D: 11 contact, double section wafer switch
- E: 11 contact, single section wafer switch
- F: 15 contact, single section wafer switch
- G: 1 Meg ohm carbon radio type potentiometer
- S-1: SPST toggle switch
- S-2: SPDT toggle switch
- S-3: SPDT toggle switch
- 1-12: banana plugs

The operation of the polarographic circuit shown as solid lines in Figure 1 is identical to that described in the paper by Watters¹¹⁹ except for the following:

(1) Galvanometer calibration. That part of the circuit shown as dotted lines in Figure 1 connecting banana plugs 7, 8, 11, 12 and potentiometer G with Aryton shunt A represents a circuit for calibrating the external galvanometer connected to plugs 1 and 2.

With switch S-3 closed to activate the calibration circuit, switch S-1 is opened and a (e.g., 22.5 volt) "B" type battery is then substituted for the usual six-volt

Fig. 1.--Polarographic bridge and galvanometer calibration circuit.

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CIRCUIT : MANUAL POLAROGRAPH

power supply at jacks 7 and 8. Selector switch D is then placed at position 8 and a calibrated 10K ohm resistor is plugged into jacks 11 and 12. The Aryton shunt, A, is placed on a suitable position, and the nominal reading is taken from the external galvanometer.

The true current flowing to the galvanometer-shunt circuit is obtained by reading the IR drop across the standard resistor at plugs 11 and 12, and the proper correction is then placed on the nominal value previously obtained.

This process may be repeated for various shunt settings on A or, alternatively, a "dummy" cell resistance (e.g., 1 meg ohm) may be connected across plugs 3 and 4, several current readings taken, and the Aryton shunt subsequently corrected, relative to itself.

If E is the voltage of the calibrating battery, e.g., 22.5 volts, and if the full 1.0 megohm resistance of G is placed in the circuit, an approximate value for the calibrating current may be obtained if a 10K ohm calibration resistor is used:

$$(34) \quad I = \frac{E_{\text{calib.}}}{10^6 + 10^4 + R_{G,S}}$$

where, $R_{G,S}$ is the resistance of the parallel network comprised of the galvanometer coil and shunt resistance. $R_{G,S}$, of course, varies with the position of the shunt, A.

According to equation (34), if $R_{G,S}$ is small (as it usually will be) compared to 10^6 ohms, and if $E = 22.5$ volts, I is approximately 22.0 microamperes. Decreasing E will decrease I , and decreasing the resistance of potentiometer G from its maximum value of 1.0 megohm will increase I . (2) Null point measurements. Positions 10 and 11 on selector switch D were added for direct null point measurement. Either one of these positions connects the measuring potentiometer directly across the polarographic cell. The two positions are "cross-connected" for measuring potentials of opposite polarity.

The electrical components which were used with the polarographic circuit shown in Figure 1 are described as follows: (1) external current measuring galvanometer. A Leeds Northrup D'Arsonval Galvanometer, Type R (Catalog number 2500), was used to measure the polarographic currents when extreme accuracy was not desired. It had a sensitivity of 0.00036 microamperes per millimeter of displacement, an external critical damping resistance of 10,000 ohms, a period of 7.2 seconds and a coil resistance of 512 ohms. Its required external critical damping resistance matched that supplied by the Ayrton shunt, A , in Figure 1.

Both anodic and cathodic currents were measured by observing the position of an illuminated circle on the frosted glass galvanometer scale which had a center zero

and extended to plus and minus 25.0 cm. (2) null point galvanometer. A Rubicon (Rubicon Co., Philadelphia, Pa.) enclosed lamp and scale galvanometer (Catalog number 3403H) was used as an integral part of the potentiometer circuit. This galvanometer had a sensitivity of 0.008 microamperes per millimeter displacement, an internal resistance of 1005 ohms, a period of 2.0 seconds and an external critical damping resistance of 6300 ohms.

In actual operation it was necessary to significantly increase the galvanometer period by shunting its terminals with a "decade" resistance box. The optimum shunt resistance for capillary drop times of 2 - 4 seconds was found to be 340 to 360 ohms. (3) potentiometer. A Leeds Northrup model K-1 potentiometer was used for measuring potentials. Its construction and operation are described in a brochure supplied by the manufacturer.

In operation the 0. to 1.60 volt range of the potentiometer was used. The potentiometer slide wire was standardized against a standard unsaturated Eppley cell whose potential was calibrated at 1.01904 volts at 25.5°C. with a similar cell whose voltage had previously been determined by the U. S. Bureau of Standards. (4) power supply. Two automobile type six-volt storage batteries were used as a power source.

One storage battery supplied the potentiometer circuit while the other supplied power to the polarographic

bridge circuit. This type of battery was chosen because its potential does not change appreciably with a small flow of current, i.e., it does not become polarized quickly. The six-volt supply to the K-1 potentiometer was first placed across a 50-ohm WW power resistor and the voltage necessary for the potentiometric slide wire then taken from the center tap.

The second six-volt storage battery was connected into the polarographic circuit via the battery jacks, 7 and 8 (see Fig. 1). These jacks were then shunted with a 1.0 megohm carbon resistor. With this resistor in place a continuous 6. microampere current drain in the battery circuit helped to prevent battery polarization from one run to the next.

Figure 2 shows a schematic arrangement of the polarograph and components. (5) grounding. Earth grounding was made to a current lead of the external measuring galvanometer, the negative side of the dropping electrode, the copper lined water bath and the aluminum front panel of the polarograph. Hence, these components were at identical potentials versus "ground". Since polarographic measurements most often involved diffusion currents of 10 microamperes or less, the exclusion of spurious potentials was deemed necessary.

Calibration of bridge circuit.--After the polarograph had been constructed, it was necessary to calibrate the

Fig. 2.--Complete Current-voltage measuring
circuit.

CURRENT-VOLTAGE CIRCUIT

potentials delivered by the bridge of fixed resistors. This was accomplished by introducing a 10K ohm, (1%) carbon-type resistor in place of the polarographic cell. The bridge current was then adjusted by means of B and C (Fig. 1) to the correct value by measuring an IR drop of 1.00000 volts between positions 4 and 9 of selector switch, F, while the switch, D, was on position 3. This should be done with switch E on "off" (position 11), so that no current will be bled off the bridge into the "dummy" cell (10K ohm resistor).

Next, shunt A was set on some convenient position, switch D turned to position 7 (positive potentials), switches E and F turned to their proper positions, and the potentials measured with the K-1 potentiometer. When negative potentials were to be measured switch D was turned to position 5.

Table 2 gives the calibration values for the 0.20 volt potential settings.

Table 3 gives the calibration values for the 0.02 volt settings.

The value of the potential increment between successive 0.20 volt values was found to be 0.200 ± 0.001 volt. The potential increment between successive 0.02 volt values was found to be 0.0200 ± 0.0001 volt. The fact that the actual incremental values are in reasonable agreement with the nominal incremental values indicates that the various

Table 2

Calibration Values for the 0.20 volt Potential Settings

$E_{\text{nominal}}(\text{volts})$	$E_{\text{observed}}(\text{volts})$	Correction(volts) $\times 10^5$
+0.4	+0.39996	-4.0
+0.2	+0.19923	-77.0
+0.0	+0.00006	+6.0
-0.0	-0.00006	+6.0
-0.2	-0.20056	+56.0
-0.4	-0.40016	+16.0
-0.6	-0.60062	+62.0
-0.8	-0.80058	+58.0
-1.0	-0.99998	-2.0
-1.2	-1.19971	-29.0
-1.4	-1.39883	-117.0
-1.6	-1.59841	-159.0
-1.8	-1.79756	-244.0
-2.0	-1.99721	-279.0
-2.2	-2.19792	-208.0

Table 3

Calibration Values for the 0.02 volt Potential Settings

E_{nominal} (volts)	E_{observed} (volts)	Correction(volts x 10^5)
$\pm$ 0.02	$\pm$ 0.02040	+40.0
0.04	0.04044	+44.0
0.06	0.06075	+75.0
0.08	0.08091	+91.0
0.10	0.10134	+134.0
0.12	0.12146	+146.0
0.14	0.14240	+240.0
0.16	0.16255	+255.0
0.18	0.18290	+290.0
0.20	0.20333	+333.0

resistances comprising the bridge are well "matched".

Although it was not really necessary, all potential values reported in this investigation are measured values, i.e., the nominal values of the potential produced by the bridge were not generally assumed to be sufficiently accurate.

Calibration of shunt.--Although the polarographic circuit as described and shown in Figure 1 contains a special circuit for shunt calibration, polarographic measurements were begun before this circuit was completed.

As an alternative and equally effective calibration

procedure, a 1%, 1.0 megohm carbon resistor and a 1%, 2500 ohm wire wound resistor were used as "dummy" polarographic cells to obtain a value for the actual current flowing in the galvanometer circuit by measuring the IR drop across these resistors with the K-1 potentiometer.

Table 4 gives the relative calibration values for the various, numbered shunt settings. In every case these values were obtained by relating the straight-line slopes of current-voltage values.

Table 4
Shunt Calibration Values

<u>Number of shunt setting (Switch A)</u>	<u>Galvanometer sensitivity: microamperes/cm deflection</u>
5	58.80
6	28.75
7	11.11
8	5.50
9	2.81
10	1.10
11	0.59
12	0.27
13	0.12
14	0.059
15	0.030
16	0.012
17	0.00059

Reference cell.--A saturated calomel electrode (S.C.E.) was used as the reference electrode in all the polarographic work of this investigation. It consisted of a

100-ml. electrolytic beaker into which was placed reagent mercury which had previously been intimately mixed with mercurous chloride. The mercury-mercurous chloride mixture was covered with a solution which had been previously saturated with both mercurous chloride and potassium chloride. A small quantity of reagent grade potassium chloride crystals was added to ensure saturation of the solution. A 7-mm. glass tube with a platinum wire sealed into one end was used to make contact with the mercury in the cell.

The standard-reduction potential of the saturated calomel electrode as a function of temperature is given by the following equation:¹²⁰

(120) J. J. Lingane, "Electroanalytical Chemistry," 2nd ed. Interscience Publishers, Inc., N. Y., 1958, p. 360.

$$(35) \quad +0.242 - 7.6 \times 10^{-4} (t - 25^{\circ}\text{C}).$$

As a check on the operational potential exhibited by this reference electrode, it was used as the reference electrode to determine the half-wave potential of the well-known thallium (I) polarographic reduction wave, which is generally known to be little affected by complexing.

The following cell was used:

where A is a 4% Agar, saturated potassium chloride salt bridge and B is a 4% Agar, saturated potassium nitrate salt bridge. The thallium nitrate was at a concentration of 2.5 millimolar; the supportant electrolyte was 0.1 molar potassium nitrate and fresh gelatin was added to a concentration of 0.005% by weight.

Lingane⁸⁶ has found an $E_{1/2}$ value of -0.459 ± 0.003 volt (25°C.) vs. S.C.E. for the thallium reduction wave (at D.M.E.) in 0.1 molar potassium chloride and also in 0.1 molar potassium nitrate. This agrees well with the value -0.461 ± 0.003 volt vs. S.C.E. (25°C.) obtained for $E_{1/2}$ potential of the thallium wave for the cell just described. This agreement, which was found in 0.1 molar potassium nitrate, does not, however, necessarily hold true for solutions of higher ionic strength, e.g., 7.5 molar potassium thiocyanate.

Polarographic cell.--Figure 3 shows the construction of the polarographic cell which was used for all quantitative work in this investigation.

The cell consisted of the saturated calomel electrode, A, described previously, which made electrical connection

Fig. 3.--Polarographic cell: (A) saturated calomel reference cell, (B) KCl salt bridge, (C) saturated KCl, KNO_3 bridge reservoir, (D) KNO_3 salt bridge, (E) working cell.

POLAROGRAPHIC CELL

to the working cell, E, via the two salt bridges, B, D, and the salt bridge reservoir, C. A 100-ml. electrolytic cell was used for A, E, and C, although, on occasion, a 180-ml. electrolytic cell was used to replace E. The bridge reservoir, C, contained a solution saturated with respect to both potassium nitrate and potassium chloride. Crystals of each of these salts were placed in the bottom of the reservoir to ensure continuous saturation.

The working cell, E, was capped with a number 10-1/2 rubber stopper drilled to accomodate the 10-mm. I.D. saturated potassium nitrate, 4% Agar salt bridge, D, the nitrogen inlet tube, the glass electrodes and the capillary tube of the dropping electrode. The sixth hole, located in the center of the cap, was used when reagents were being added to the working cell during a particular run. If a buret were used for this purpose, its off-center tip was placed through the center hole.

The beakers comprising the entire cell shown in Figure 3 were held in place in the water bath by universal clamps, which were fastened to a metal rod framework built over the water bath. The 10-mm. I.D., saturated potassium chloride 4% Agar salt bridge, B, was left permanently in place while the potassium nitrate bridge, D, was removed between runs and placed in a desiccator filled with saturated potassium nitrate.

Many of the polarographic runs in this investigation

were made in very concentrated (7.5 molar) potassium thiocyanate solutions which had a tendency to loosen the Agar in the end of the potassium nitrate bridge. Whenever this happened, a new, similar salt bridge was constructed.

Polarographic capillaries.--The capillaries used to obtain polarographic data in this work were of the Sargent "2 - 5 second" polarographic type (E. H. Sargent & Co., Chicago, Ill., Catalog number S-29419), and were used as received.

Capillary characteristics, $m^{2/3}t^{1/6} = mg^{2/3}\text{second}^{-1/2}$, were always obtained with the particular capillary dropping into the test solution. Values for the mass of mercury (amalgam) flowing per second, $m = \text{mg/sec.}$, were obtained by allowing the electrode to drop continuously into the test solution for a period of time not less than one-half hour. The time during which the mercury (amalgam) flowed was measured accurately to one-hundredth minute by an electrical timing device (Precision Scientific Co.). The working cell containing the small pool of mercury or amalgam was then removed, and the metal washed several times with distilled water, dried thoroughly with acetone and weighed on the analytical balance.

The drop time, t , of the capillary was measured with a conventional stopwatch and was computed as the average time it took for 10 drops to fall from the capillary tip. Drop times were always measured while the dropping

electrode was under a definite, applied potential. Upon finishing a polarographic run, the capillaries were washed copiously with distilled water, wiped dry with tissue, and in the case of the dropping mercury electrode, the mercury flow was shut off by means of the stopcock located directly above the capillary. The dropping amalgam electrode, however, after being washed and dried thoroughly, was allowed to drop continuously under a reduced pressure into either ethanol or distilled water acidified with hydrochloric or nitric acid. It was found that this procedure was necessary to prevent clogging of the tip which otherwise would become blocked with oxide in the presence of distilled water only.

Water bath.--A rectangular water bath having inside dimensions of 57 cm. x 32 cm. x 41 cm. and a capacity of 74.8 liters was used to control the temperature in all polarographic experiments.

The water bath was constructed with a copper lining surrounded on all sides with powdered mica to reduce heat transfer. The whole was housed in a wooden box-like construction. Temperature control and stirring were accomplished by an E. H. Sargent heater-pump and Thyatron type thermoregulator (Catalog number S-84805).

Dropping amalgam reservoir and standtube.--The dropping amalgam reservoir and its associated standtube were fabricated entirely of glass in this laboratory by Mr. William

Leonard. The basic design for this instrument was patterned after that first reported by Cooper and Wright¹²¹ and

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

later used by Furman and Cooper.¹¹¹

Figure 4 shows a modified version of their instrument which was used in this investigation. The principal changes included the addition of a two-way ground-glass stopcock at the bottom of the round, 150-ml. reservoir. After preparation, the amalgam was introduced into the reservoir through the side tube of this stopcock.

Instead of fastening the capillary to the reservoir with a glass seal, it was fastened with Varno cement (Varniton Company, California) to the "female" member of a $\text{E } 12/30$ ground glass joint. The assembly was then connected to the "male" member of the $\text{E } 12/30$ joint which was located directly below the lower stopcock on the reservoir. The tapered joint was wired securely in place to ensure against its subsequent separation under the pressure of a large head of amalgam. Under similar experimental conditions the $\text{E } 24/40$ joint holding the standtube in place at the top of the reservoir was also securely wired.

Prior to the preparation of each amalgam, the all-glass reservoir and associated standtube were scrupulously

Fig. 4.--All-glass dropping amalgam reservoir
and associated standtube assembly.

cleaned according to the following, unvarying procedure: (1) rinsed with water to remove loose particles of oxide and amalgam; (2) washed thoroughly with acetone to remove mineral oil, grease, etc.; (3) cleaned with cold chromic acid, then flushed copiously with tap water; (4) rinsed with distilled water, then acetone and finally, (5) air dried. During this cleaning procedure, the keys were removed from the stopcocks, and the coating of Cello-Grease removed with acetone; the keys were then regreased.

Reagents and chemicals.---The "specpure" gallium and indium metal which was used to prepare the amalgams was obtained from Johnson, Matthey & Co., Ltd. These metals were accompanied by the firm's analytical report (see Appendix V) which listed all the impurities, expressed as parts per million, which could be detected spectroscopically.

Gallium nitrate octahydrate and indium chloride were also obtained from Johnson, Matthey & Co., Ltd. as the "specpure" salts (see Appendix V). One hundredth molar stock solutions of these reagents were prepared directly from the "as received" salts. The gallium nitrate had a tendency to be somewhat deliquescent, but several trial weighings of this salt indicated that the amount of moisture picked up during a typical weighing operation was experimentally negligible.

Stock solutions (0.01 molar) of indium nitrate were

prepared directly from indium metal by dissolving a weighed quantity of the "specpure" indium in a known weight of previously boiled, concentrated reagent grade nitric acid. An excess of acid was added to ensure complete reaction of the indium and to suppress the strong tendency of In^{+3} to hydrolyze. In preparing the gallium nitrate stock solutions, however, no attempt was made to suppress hydrolysis.

Reagent grade mercury was used to prepare the dropping amalgams and for the dropping mercury electrode. When used for amalgam preparation, the reagent mercury was "pinholed" through filter paper at least once to remove the small amount of oxide and surface scum.

All other chemicals which were used in this work were of the "analyzed" reagent grade, except for the maximum suppressors which were ("chemically pure") i.e., C.P. grade.

The 10.0 M stock solutions of potassium thiocyanate were standardized volumetrically with silver nitrate, using eosin as the indicator. Although polarographic residual current waves obtained with solutions containing the stock potassium thiocyanate did not show the presence of reducible impurities, it was decided to check on this possibility, since impurities might easily affect the polarographic behavior of Ga^{+3} . Reagent grade potassium thiocyanate was recrystallized twice at 0.0°C. from saturated,

demineralized, double distilled water. Polarographic reduction waves of Ga^{+3} obtained in the presence of the twice recrystallized salt did not differ from those obtained using the stock potassium thiocyanate.

Water.--Demineralized, double distilled water was used exclusively throughout this investigation for the preparation of all solutions.

Temperature control.--All quantitative polarographic measurements were obtained under the condition of strict temperature control. The temperature of the water bath was maintained at $25.0 \pm 0.1^{\circ}C$. either by increasing its temperature by means of the previously described pump-heater or lowering it by blowing the stream of air from an ordinary electric fan across the water's surface.

Nitrogen.--The inert gas which was used without further purification to "outgas" the polarographic test solutions and to exclude air in the preparation and use of the amalgams was Linde "High Purity," dry pumped tank nitrogen.

CHAPTER IV

PREPARATION OF AMALGAMS

Gallium.--Gallium amalgams were prepared by dissolving a weighed quantity of solid, oxide-free gallium metal in a weighed quantity of reagent grade mercury. The gallium metal, as received, was in the form of small, gray-colored pellets of varying size which weighed but a few milligrams each. The operational procedure which was finally developed for preparing the dilute amalgams (0.0002-0.0024% gallium by weight) was as follows:

Two or three gallium pellets of approximately the correct weight (previously determined) were placed on a two-inch watch glass containing enough 1.0 molar hydrochloric acid to completely cover the pellets. The watch glass containing the pellets covered with acid was then placed close under a lighted 100-watt electric light bulb. The heat radiated by the bulb soon melted (at $29.75^{\circ}\text{C}.$) the pellets of gallium. Immediately on melting, the oxide layer which covered each pellet dissolved, leaving a bright, shiny globule of gallium. The globule of melted metal was then transferred immediately to a second watch glass containing ethanol whose temperature had previously been lowered to $16^{\circ} - 20^{\circ}\text{C}.$ by its own evaporation.

Upon being immersed in the cold ethanol, the gallium globule immediately solidified producing, as a result, a hard, shiny pellet of gallium which, to all appearances,

was free of an oxide coating. If handled carefully, with clean polyethylene forceps, the pellet could be weighed conveniently on an analytical balance. After being weighed, the pellet was placed in a 250-ml. vacuum filter flask containing 1000.0 grams (about 75 ml.) of reagent grade mercury which had been previously evacuated and washed with nitrogen, 4 - 5 times.

The entire operation of placing the gallium pellet into the filter flask was carried out with the exclusion of air by dropping the pellet through the large, top opening against a stream of nitrogen which was entering the flask through its side arm. After one or two minutes, the gallium dissolved. The flask was then closed with a rubber stopper containing a vacuum stopcock in the closed position. The flask was evacuated and then shaken periodically for about an hour to mix the amalgam.

The vacuum flask containing the amalgam was subsequently inverted and connected by a length of new, dry Tygon tubing to the side opening of the bottom stopcock of the amalgam reservoir. The reservoir and standtube assembly had been previously cleaned (following the procedure already described) and "washed" several times with High Purity nitrogen. The reservoir assembly and connecting Tygon tubing were then evacuated to the limit of the pump.

It was found necessary to have the entire system at reduced pressure while the amalgam was being transferred to the reservoir: (1) to minimize the presence of oxygen which would attack and destroy the amalgam, (2) to prevent gas locks in the area immediately above the capillary, and (3) to hasten the transfer of liquid metal by slowly leaking N_2 gas into the side arm of the inverted vacuum flask.

When the entire assembly had been evacuated, the stopcock on the inverted vacuum flask was very slowly opened, and a small steady stream of amalgam allowed to pass down the Tygon tube into the reservoir. After about 5 ml of metal had passed, the lower stopcock on the reservoir was reversed and the liquid metal allowed to drop into the tube above the capillary. This tube was then tapped sharply several times to destroy any metal separation that might have occurred. This procedure was repeated until the lower tube was completely full and a solid metal connection made through the open stopcock into the lower reservoir. The stopcock was then reversed, and the remaining quantity of amalgam transferred into the reservoir.

During this phase of the operation, the entire system was maintained at reduced pressure by continuous evacuation. After the amalgam was transferred, the system was carefully brought up to atmospheric pressure by slowly bleeding High

Purity nitrogen gas into the reservoir through its upper stopcock. The nearly vertical tube of the upper reservoir stopcock was subsequently filled with C.P. mineral oil, and this was driven into the reservoir with nitrogen gas. The careful, step-wise addition of mineral oil to the reservoir was repeated until the amalgam surface was completely covered. The dropping amalgam electrode was now ready for use.

When prepared according to this procedure, the amalgam remained stable but maintained its nominal concentration - as indicated by the anodic diffusion current - only if it were allowed to drop continuously between successive runs.

Indium.--Except for the preliminary treatment of the metal, indium amalgams were prepared in a manner analogous to that of the gallium amalgams just described.

The indium metal, as received, was in the form of soft wire (see Appendix V), and could be cut easily with a clean steel knife into small pellets having freshly exposed, oxide-free surfaces. These small pellets, without further treatment, were weighed on an analytical balance, and the amalgam was then prepared according to the procedure for gallium.

CHAPTER V

EXPERIMENTAL PROCEDURE

The polarographic measurements which were made in this investigation always followed an operational procedure of which the following is most typical: approximately two hours prior to the time actual current-voltage measurements were to begin, the polarographic circuit was turned on by means of toggle switch S-1 (Fig. 1); and S-2, S-3 were turned to their appropriate positions. This "warm-up" period was found necessary to (1) allow the ratio potentiometers, B and C, to come to temperature equilibrium, and (2) allow the storage batteries to stabilize their potentials.

At the time the polarograph was turned on, the water bath Thyatron control was also turned on, and the bath brought up (or down) to a temperature of $25.0 \pm 0.1^\circ\text{C}$. While the bridge circuit was warming up, the stock test solutions (usually 100-ml. volumes) were made up from the previously prepared stock material. A thirty to fifty milliliter volume of test solution was then pipetted (10-ml., blue-line Exax pipet) into the 100-ml. electrolytic test cell (see Fig. 3). The 6-hole stopper was put in place, and the 10-mm., saturated, potassium nitrate, 4% Agar salt bridge inserted into the cell and bridge reservoir. The "L-shaped" nitrogen bubbler tube was then inserted, and the solution outgassed slowly for 30 - 60 minutes with High Purity nitrogen.

The dropping amalgam (or dropping mercury) electrode was rinsed with distilled water, wiped dry with tissue and then inserted into the working cell. The capillary was immersed in the test solution, usually to a depth of about 1 cm., and the amalgam or mercury adjusted to an appropriate height (usually 60 - 80 cm.) in the standtube. When the dropping amalgam was used, its hydrostatic pressure (height) was adjusted by increasing the nitrogen pressure in the reservoir - the operation was carried out using Tygon tubing which had been previously flushed with High Purity nitrogen gas to prevent the introduction of oxygen into the reservoir.

The output leads from jacks 3 and 4 on the manual polarograph were then connected to the saturated calomel electrode and to the platinum contact of the dropping electrode. Selector switch D (Fig. 1) was turned to position 3, switch E to "off" (position 11), and the K-1 potentiometer then set at 1.00000 volt. Bridge resistances B and C were adjusted to give an exact balance of the potentiometer, as indicated by the Rubicon galvanometer. At balance a current of about 0.04 ampere, which flowed through the resistances comprising F, produced a 2.8000 volt potential drop across positions 1 and 15.

With this done, switch F was set at some nominal potential corresponding to the diffusion current of the wave, and the Aryton shunt, A, was then set at a value

which would keep the current measuring galvanometer "on scale" (position 10 allowed the correct current to be read directly from the galvanometer scale).

When current-voltage measurements were begun, switch D was set at either position 5 for cathodic potentials, or position 7 for anodic potentials as the situation demanded; the potentials were nominally applied in 0.20 volt and 0.02 volt increments, but were actually measured with the K-1 potentiometer. Currents corresponding to each potential were measured with either the external galvanometer or as the I.R. drop across the 1%, WW 2500 ohm or 10,000 ohm resistors of switch A.

Bridge potentials which were applied to the cell in excess of 1.60000 volt, the upper limit of the K-1 potentiometer, were measured by setting selector switch D on position 1. With the selector switch in this position, the polarity of the potentiometer was reversed, and I.R. drops across positions (switch F) higher than number 9 were measured. In this instance the true, applied potential equaled the measured potential plus 1.00000 volt.

At applied potentials which were very negative, large current oscillation often made the measurement of potentials difficult. When this happened toggle switch S-2 was reversed, that is, an 80,000 ohm series resistor was placed in the circuit, which had the effect of damping the galvanometer oscillations. Current-voltage data which

were obtained in this way were corrected for the (non electrolytic) internal resistance of the solution whose measurement has already been described in Chapter III. The I.R. corrections were subtracted from the measured potentials of cathodic waves and added to those of anodic waves. Thus, the positive slope of the measured C-V curve was increased slightly as a result of these corrections.

CHAPTER VI

DISCUSSION OF RESULTS - I. GALLIUM

Dropping gallium amalgam electrode.--At the time this investigation of the electrochemistry of gallium was begun, there was no knowledge available to indicate that a dropping gallium amalgam electrode had been used to obtain anodic or composite polarographic waves.

Some early work¹²² indicated that gallium and mercury

(122) Ramsay, Loc. cit.

are not mutually soluble at room temperature. Stelling's work,³¹ however, showed that a dropping gallium amalgam could be used to determine a reproducible electrode potential for the gallium couple in chloride media. Stelling worked with amalgams of concentrations of 0.25 to 0.05% by weight, which he prepared by dissolving liquid gallium in mercury. He freed the gallium of surface oxide by passing it through a capillary tube in a hydrogen atmosphere. He noticed that an oxide coating slowly formed on the amalgam surface after a period of several hours which, however, did not appear to affect the measured null potentials.

Preliminary trials were made in this investigation to determine the ease with which gallium would dissolve in mercury at room temperature. It was found that the solid, "as received" pellets of "specpure" gallium would

not dissolve (or at most only slowly) in mercury. This behavior seemed to suggest that a gallium oxide layer was preventing the mercury from wetting the gallium pellet.

Subsequent treatment of the gallium pellets with warm hydrochloric acid followed by freezing in ethanol not only cleaned the oxide from the gallium but resulted in a hard, shiny pellet which could be handled and weighed with no difficulty as long as the ambient temperature was below the melting point of gallium ($29.75^{\circ}\text{C}.$). On contact with mercury the oxide-free pellet was found to dissolve rapidly, but in the presence of air the dissolved gallium quickly turned to oxide which formed as a thick, gray coating on the mercury surface.

A gallium amalgam which was prepared by dissolving 0.065 gms. of oxide-free gallium in 1000.0 gms. of air-free mercury in an unpurified hydrogen atmosphere soon showed a coating of gray oxide in spite of rigorous attempts to exclude air from the system. When used as a dropping electrode immediately after its preparation, the 0.0065% gallium amalgam yielded an anodic polarographic wave saturated potassium nitrate whose diffusion current was in excess of 100 microamperes.

Twenty-four hours later, the diffusion current was zero, and the amalgam was covered with a thick coating

of oxide. It was concluded that the unpurified tank hydrogen contained a small percentage of water vapor or oxygen which ultimately caused the destruction of the amalgam.

The procedure for preparing the gallium amalgams was then altered by substituting Linde "High Purity," dry pumped nitrogen - without further purification - for the ordinary commercial grade tank hydrogen. As an additional precaution, C.P. grade mineral oil was used to cover the amalgam surface in a thin layer to minimize contact of the amalgam with the "inert" gas in the reservoir. This procedure worked well. The amalgams which were treated in this way remained free of noticeable oxide during the entire length of time they were used.

Data were obtained from two series of amalgams: The first series, comprised of four amalgams which were numbered I to IV, gave semi-quantitative information regarding the polarographic character of the gallium anodic and composite waves, but, more importantly, this series yielded information with regard to the stability, optimum concentration range and preparative procedure which was subsequently applied when quantitative polarographic measurements were obtained.

The second series of amalgams, numbered V to XII, was used with the all-glass apparatus which has already been discussed.

Table 5 summarizes the behavior of the amalgams comprising the first group.

Table 5
Dropping Gallium Amalgams - Series I

Number	Nominal Concentration		Approximate Anodic
	Moles/liter (Amalgam)	% Ga by weight	Diffusion Current (Amperes)
I	4.3×10^{-3}	2.3×10^{-3}	56.5×10^{-6}
II	5.1 "	2.7 "	68.5 "
III	6.1 "	3.2 "	62.0 "
IV	5.5 "	2.9 "	54.0 "

The amalgams of both groups were prepared in exactly the same fashion. They differed, however, in concentration and in type of electrode assembly with which they were used. Whereas those of the second group were housed in an all-glass reservoir assembly, those of the first series were used with an ordinary leveling bulb reservoir which was connected to a standtube and capillary with a long piece of new, dry Tygon tubing. This arrangement was filled with High Purity nitrogen and made a closed system by connecting together the tops of the standtube and leveling bulb with Tygon tubing.

Although every precaution was taken to exclude oxygen from the system, it was noticed that every amalgam of the

first group began to decrease in gallium content - measured as the anodic diffusion current - soon after preparation, and within five to six days yielded no anodic current at all. It was significant that soon after preparation every one of the first four amalgams showed a white oxide layer on the inside surface of the Tygon tubing which connected the reservoir with the standtube, but that no oxide was visible in the glass portions of the apparatus. This oxide coating grew thicker with time, and appeared to parallel the decomposition of the amalgam.

It was tentatively concluded that a property of the Tygon itself, perhaps its permeability to oxygen or its affinity for water vapor, was responsible for the destruction of the amalgam. This conclusion was confirmed when the amalgam was prepared and used in the all-glass reservoir and standtube. It was found that the glass assembly preserved the amalgam indefinitely with no indication of oxide formation.

The high concentrations of gallium used in Amalgams I through V yielded anodic currents which were too large for quantitative polarographic measurements and often caused erratic drop times owing to the frequent, partial plugging of the capillary tip with oxide. Streaming of the amalgam drop was often observed at the higher amalgam concentrations, but, since cleaning the capillary tip with hot 1:1 nitric acid restored the normal drop rate,

it was concluded that this streaming was due to a partial obstruction of the tip. For these reasons it was decided to use much lower gallium amalgam concentrations (see Table 6).

Several trial preparations of the amalgam indicated that a concentration of 0.0002(0)% by weight gallium was optimum.

Table 6 summarizes the data for amalgams V to XII.

Table 6

Dropping Gallium Amalgams - Series II

Number	Nominal Concentration		Approximate Anodic
	Moles/liter (Amalgam)	% Ga by weight	Diffusion Current (Amperes)
V	4.5×10^{-3}	2.4×10^{-3}	54.4×10^{-6}
VI	1.6 "	0.85 "	(13.3) ^a "
VII	1.6 "	0.80 "	-- b
VIII	2.4 "	1.2(3)"	27.5 "
IX	1.0 "	0.54 "	(10.2) ^c "
X	0.80 "	0.42 "	13.5 "
XI	1.1 "	0.59 "	18.9 "
XII	0.38 "	0.20 "	4.0 "

a: Oxygen entered system when capillary was replaced.

b: Varro seal cracked, spilling amalgam - no data taken.

c: Possible air leak through capillary when transferring amalgam.

Amalgams VI, VII, VIII were accidentally destroyed soon after transferring them to the all-glass reservoir, because the Varno cement holding the capillary cracked, spilling the amalgam and introducing oxygen into the system before the lower stopcock could be closed. It was subsequently found that excessive and repeated heating of the low-melting cement when forming the seal caused it to become brittle and crack under slight pressure. When fresh, only slightly warmed cement was used, this difficulty was not encountered, and the seal remained intact under high pressure.

The behavior of the amalgams in series II soon demonstrated a peculiar phenomenon which has not, as yet, been satisfactorily explained. It was noted that the anodic diffusion current, and, hence, the amalgam concentration, remained constant between runs only if the amalgam electrode were allowed to drop continuously from the reservoir. If the capillary became plugged for several hours, or if the stopcock above the capillary were shut off overnight, the anodic diffusion current fell to a very low value, often to zero, then increased steadily with time until it reached its former constant value. Amalgam XI behaved in this manner after its capillary tip became temporarily clogged with oxide.

Two possible explanations for this phenomenon suggest themselves: (1) When the amalgam has ceased to flow, that

part of it contained in the small space between the capillary and the lower stopcock may be "leached" through reaction with stopcock grease or small amounts of moisture trapped in the small crevasses near the Varno seal. This explanation was supported by the fact that when amalgam flow began, the anodic current was restored after a quantity of metal had passed through the capillary approximately equal to the volume of space between the capillary and lower stopcock. (2) Since the density of gallium is only about one-half that of mercury (5.9 gms./cm^3 compared to 13.55 gms. cm^3 for mercury at room temperature), long standing might produce a gallium concentration gradient in the amalgam. Thus, the initial loss in anodic current would be accounted for, but, since the amalgam in the reservoir should be equally affected, this simple mechanism cannot explain the subsequent increase of the current to its former value.

Polarography in KNO_3 .--To obtain useful quantitative polarographic measurements of the gallium couple in the presence of complexing anions it was first necessary to have a knowledge of its behavior in non-complexing media.

Qualitative measurements obtained with amalgams I through XI had indicated the presence of a well-defined anodic wave in solutions containing potassium nitrate. Because the magnitude of the anodic currents of these early amalgams was so large, an accurate measurement of the

cathodic wave at low galvanometer sensitivity proved difficult.

Figure 5 shows the polarographic "spectrum" which was obtained with amalgam XII (0.0002% by wt. gallium) dropping into an air-free solution 0.1 molar in potassium nitrate, which also contained 0.0005 molar gallium nitrate and 0.005% fresh gelatin. Three distinct polarographic waves are evident in Figure 5: (1) First the large anodic wave is well-defined and has a diffusion current of -4.0 microamperes. This wave corresponds to the three-electron oxidation of the gallium in the amalgam drop,

and has an $E_{1/2}$ (which was obtained graphically from the curve in Figure 5) of -0.76 volt vs. S.C.E.

The concentration of amalgam XII, 0.0002% by weight in gallium, when converted in the usual way, corresponds to a concentration of 3×10^{-5} molal.

If the standard oxidation potential of +0.58 volt vs. N.H.E., which was obtained by Challenger¹² for the liquid metal at 29.75°C., and an amalgam concentration of 3×10^{-5} molal are properly substituted into the Nernst equation for reaction (36) at 25°C., then,

$$(37) \quad E_{\text{Ga(Hg)}} = E_{\text{Ga,Ga}^{+3}}^{\circ} - \frac{.0591}{3} \log \frac{a_s}{a_a}$$

Fig. 5.--Anodic-cathodic wave taken of a solution 0.5 millimolar in $\text{Ga}(\text{NO}_3)_3$, 0.1 molar in KNO_3 and 0.005% in fresh gelatin (amalgam XII: 0.0002% in Ga). Dotted portion of curve represents data taken from the automatic recording polarograph ($m^{2/3}t^{1/6} = 2.125 \text{ mg}^{2/3}\text{sec}^{-1/2}$ at -1.20 volts vs. S.C.E.).

$$(38) \quad E_{\text{Ga(Hg)}} = +0.58 + 0.02 \log 3 \times 10^{-5} - 0.02 \log a_s.$$

Therefore, at $a_s = 1.0$ molar,

$$(39) \quad E_{\text{Ga(Hg)}} = E_{\text{Ga(Hg)}}^{\circ} = +0.58 + (-0.09) = +0.49 \text{ volt vs. N.H.E.}$$

Compared with the saturated calomel electrode, whose potential is given by equation (35), the reduction potential obtained for $E_{\text{Ga(Hg)}}^{\circ}$ from equation (39) would be equal to -0.73 volt. Since equation (20) indicates that the standard reduction potential (E°) and polarographic half-wave potential ($E_{1/2}$) are very often of closely comparable value, the experimentally obtained potential of -0.76 volt vs. S.C.E. for reaction (36) compares favorably with the "theoretical" value of -0.73 volt vs. S.C.E. in spite of the fact that the latter value was arrived at by neglecting the activity coefficient of gallium in the amalgam. The experimental value of -0.76 volt vs. S.C.E. includes an unknown junction potential which was estimated to be no more than 3. millivolts; (2) Figure 5 shows, in addition to the anodic wave, two cathodic waves which correspond favorably to those obtained by Challenger¹² for 0.5 millimolar gallium chloride in 0.1 molar potassium chloride containing 0.005% gelatin.

Zittel⁴² unknowingly confirmed Challenger's work in this medium, but he failed to mention the presence of the second wave which Challenger attributed to the hydrogen

ion resulting from the natural hydrolysis of Ga^{+3} . The drawn out character of the first cathodic wave in Figure 5 confirms the conclusions of both Challenger¹² and Zittel,⁴² who showed that a plot of E_{applied} vs. $\log \frac{1}{i_d - i}$ for this wave gave a reciprocal slope (0.08 to 0.09 volt) which was nearly four times too large for a reversible three electron reduction of trivalent gallium. They postulated that this irreversible wave may indicate disproportionation of Ga^{+2} to the metal. That the first cathodic wave corresponds to trivalent metal reduction, was shown by Zittel who performed accurate coulometric measurements in this potential range.

Graphical measurement to determine the half-wave potentials of the first and second cathodic waves gave values of -1.05 and -1.50 volts vs. S.C.E. respectively. These values compare well with -1.11 and -1.51 volts vs. S.C.E. obtained by Challenger for 0.5 millimolar Ga^{+3} in potassium chloride.

Table 7 compares the results obtained in this work with those reported by Challenger.

Table 7

Comparison of Gallium Cathodic Polarography

	<u>This Work</u>	<u>Challenger</u>
G_a^{+3} (moles/liter)	0.0005 M $Ga(NO_3)_3$	0.0005 M $GaCl_3$
Supporting electrolyte	0.1M KNO_3	0.1 M KCl
gelatin	0.005%	0.005%
i_d (amperes $\times 10^{-6}$)	4.06 ^a (at -1.3 volts)	3.81
$m^{2/3}t^{1/6}$ ($mg^{2/3}t^{-1/2}$)	2.125 (at -1.2 volts)	1.98
$\frac{i_d}{cm^{2/3}t^{2/6}} = I$	3.84	3.85
$E_{1/2}$: <u>vs.</u> S.C.E. (25°C.)	-1.05 volts	-1.11 volts

a: Corrected for a residual current of 0.19 micro-amperes at this voltage.

The data as plotted in Figure 5 indicate that the difference in half-wave potentials of the anodic wave and cathodic wave, i.e., the overpotential, is about 0.29 volt.

Challenger found, and it was confirmed in this investigation, that increasing the gallium concentration caused the cathodic $E_{1/2}$ to move to more negative values vs. the saturated calomel electrode, until the reduction wave merged with the hydrogen wave. Thus, since the anodic wave is essentially independent of the solution composition, the polarographic overpotential for the gallium couple

would be greater at high gallium concentrations. This would seem to confirm early observations which indicated that gallium could not be electroplated easily from "neutral" or acid solutions.

The Ga^{+3} hydrolysis wave which is evident in Figure 5 is of special significance, for, since it is a measure of the hydrogen ion concentration resulting from hydrolysis, it should provide a means of calculating an estimate of the hydrolysis constant if the hydrolysis reaction is limited to one step.

This type of wave is not at all uncommon. Kolthoff and Lingane¹²³ have reviewed the subject of hydrolysis

(123) Kolthoff and Lingane op. cit. p. 115.

waves, and have cited Cr^{+3} as an example of an ion yielding such a wave. Some comparison studies of the polarography of In^{+3} which were conducted as a part of this investigation have shown that this ion also yields a polarographic wave corresponding to its natural hydrolysis. This subject will be subsequently pursued in Chapter VIII in connection with the calculation of hydrolysis constants from polarographic data.

Polarographic maxima.--Upon commencing the study of gallium polarography, both with the dropping gallium amalgam and with the dropping mercury electrode, it was soon

evident that anodic and cathodic maxima would need to be suppressed. Figure 6 shows a flat type of anodic maximum which was obtained with the dropping amalgam electrode (0.0027% gallium) in potassium nitrate. This plot also shows the deleterious effect on the anodic wave of adding Triton X-100, a commercial surface active agent. With concentrations of Triton X-100 sufficient to entirely suppress the maximum it can be seen that the anodic $E_{1/2}$ was shifted to more positive values. Because of this behavior, Triton X-100 was abandoned as a maximum suppressor in favor of freshly prepared gelatin in concentrations of 0.01% by weight or less which did not shift or depress the anodic wave. It was later found that gelatin was equally effective in suppressing the cathodic maxima.

Figure 5 is an indication of the effectiveness of 0.005% gelatin in suppressing the anodic maximum in 0.1 molar potassium nitrate.

In contrast to the flat type of maximum found in potassium nitrate, Figure 7 shows a pronounced rounded maximum which was obtained with the dropping amalgam electrode (0.0023% gallium) in 1.0 molar hydrochloric acid.

Amalgam polarography in the presence of salicylic acid, which will be discussed in a subsequent section, showed the unusual phenomenon of simultaneously occurring

Fig. 6.--Anodic, flat maxima in KNO_3 and the effect of Triton X-100 on the anodic wave (amalgam II : 0.0027% Ga; Triton X-100 : 0.8 to $2.0 \times 10^{-3}\%$).

Fig. 7.--Anodic maximum in 1.0 molar HCl (amalgam I :
0.0023% Ga).

anodic and cathodic maxima. These maxima could be suppressed by the addition of 0.01% gelatin or Triton X-100.

Gallium polarography in the presence of complexing anions.--It is quite generally known⁷⁰ that the polarographically irreversible reduction of a completely solvated cation may be improved or oftentimes made completely reversible by the addition of a complexing anion to the system. A very good example of this behavior is the reversible reduction of the chloro complex of trivalent indium, the aquo "complex" of which yields a very irreversible polarographic reduction wave.^{54,72,124} The

(124) Kolthoff and Lingane op. cit. Vol. II, p. 519.

polarographic behavior of the solvated gallium ion is quite similar to that of indium.

Prior investigations^{12,41,42,43,46,47,48,49} have surveyed the effect of some anions on the irreversible reduction behavior of gallium. These investigations have shown that the following anions have no improving effect: fluoride, chloride, bromide, iodide, nitrate, sulfate, perchlorate, tartrate, acetate, citrate, sulfosalicylate, and ethylenediaminetetraacetic acid (EDTA, Trilon). The results of the present investigation have qualitatively confirmed this observation for fluoride, chloride, bromide, iodide, nitrate, tartrate, acetate and EDTA. In addition

the same negative effect has been observed for malonate, formate, oxalate and phthalate.

When making qualitative observations of the effect of complexing anions on gallium polarography, the dropping gallium amalgam electrode had a special advantage over the dropping mercury electrode, because any tendency to form a complex gallium ion was immediately reflected in a shift to more negative potentials of the gallium anodic wave. Such a shift was definitely noted in gallium solutions containing formate, fluoride or EDTA. Although this particular shifting effect was not further investigated, it appears that it could yield a good method for expanding the present sparse knowledge¹²⁵ concerning gallium com-

(125) J. Bjerrum, et al., "Stability Constants," Vol. II, The Chemical Society, London, 1957.

plexity constants. On the basis of early investigations it thus appeared that gallium polarography was somewhat unique in not being affected, at least partially, by the presence of complexing anions.

Vinogradova and Chudinova⁴⁶ reported, in 1956, that reduction of trivalent gallium at the dropping mercury electrode was enhanced sufficiently in the presence of thiocyanate buffered with salicylic acid to allow the quantitative determination of that metal, provided methanol

was added to suppress the cathodic maximum. This work was followed the next year by that of Zelyanskaya and Bau-sova^{47,48} who reported that they had determined gallium polarographically at the dropping mercury electrode in a solution which was 0.1 molar in sodium salicylate.

The results of these two investigations, when compared, suggested that the salicylate ion alone could be responsible for the improved behavior of the gallium reduction. Polarographic experiments were then run to check the individual effect of salicylate and thiocyanate ions on the reversibility of the gallium couple. It was subsequently found that the presence of each anion alone moved the gallium half-wave potential to more positive values and yielded a well-defined polarographic reduction wave. The presence of thiocyanate as the potassium salt seemed, however, to have a greater salutary effect on the wave than did the presence of salicylate.

It was evident from the small shift in the anodic $E_{1/2}$ potential upon using larger concentrations of anion, that, if a gallium complex ion were being formed, its complexity constant must be small. Since the effect of thiocyanate on the gallium couple was not as well known as that of salicylate, and because the high aqueous solubility of potassium thiocyanate permitted a very large thiocyanate to gallium concentration ratio in solution, it was chosen for further investigation.

Gallium polarography in thiocyanate media.--Figure 8

shows the variation of the gallium reduction wave caused by an increase in thiocyanate concentration. Data for these curves were obtained using a mercury electrode ($m^{2/3}t^{1/6} = 2.403 \text{ mg}^{2/3}\text{sec}^{-1/2}$ at -1.2 volts vs. S.C.E.) dropping into a test solution containing 0.5 millimolar gallium nitrate whose ionic strength, μ , was controlled at 0.5 molar with potassium nitrate.

The curve represented by half-solid circles is the residual current data for which all the waves were corrected. It is to be noted that a reduction wave for 0.5 millimolar gallium nitrate is not evident in 0.5 molar potassium nitrate. This conforms with Zittel's⁴² observation that an increase of ionic strength shifts the wave for uncomplexed Ga^{+3} to more negative potentials. A slight inflection indicating the presence of a reduction wave is noticeable at $\text{SCN}^- = 0.09$ molar. The wave is definite at $\text{SCN}^- = 0.40$ molar and well-defined at $\text{SCN}^- = 0.50$ molar. The curve representing the data taken at $\text{SCN}^- = 0.20$ molar appears to be anomalous. Up to a potential of -1.1 volts vs. S.C.E. this particular curve behaves normally. Past this potential, however, its general shape resembles those curves taken at lower thiocyanate concentrations. If the data taken at $\text{SCN}^- = 0.20$ molar are interpreted correctly, a transition appears to take place in the system between 0.20 and 0.40 molar thiocyanate.

Fig. 8.--Variation of Ga^{+3} cathodic diffusion current with increasing KSCN concentration (ionic strength held constant at 0.5 molar). Curve designated by half-solid circles represents residual data taken in 0.5 molar KNO_3 .

Composite.--As previously discussed, a composite wave whose description is given by equation (20) represents the best experimental test for polarographic reversibility.

The dropping gallium amalgam electrode was used initially, therefore, to determine to what extent the presence of thiocyanate affected the polarography of the gallium couple. In these experiments the chief interest was to determine whether or not the polarographic current inflected as it crossed the zero current axis in going from the anodic to the cathodic region.

Figure 9 is a typical curve showing the qualitative behavior of 5.0 millimolar gallium nitrate at the dropping amalgam electrode (0.0024% gallium). The test solution used to obtain this polarogram was 0.1 molar in potassium nitrate, contained 0.0024% gelatin and exhibited a "natural" pH of 3.4. The data represented by Figure 9 was obtained at 1.0 molar potassium thiocyanate.

The curve shown in Figure 9 exhibits a well shaped anodic wave whose current crosses the zero current axis uninflected to form two well-defined cathodic waves representing, respectively, the reduction of some species of gallium and the reduction of hydrogen resulting from the hydrolysis of trivalent gallium.

There are several points of interest to be noted in these waves: (1) while the anodic $E_{1/2}$ in 1.0 molar

Fig. 9.--Composite Ga wave. Test solution:
5 x 10⁻³ molar Ga(NO₃)₃ in 1.0 molar KSCN containing
0.1 molar KNO₃ and 0.0024% gelatin. (Amalgam V : 0.0024%).

potassium thiocyanate is shown to be -0.84 volt vs. S.C.E., it was later found to be -0.86 volt vs. S.C.E. in 2.0 molar potassium thiocyanate - a definite negative shift. This behavior indicates that Ga-SCN complex formation may be occurring; (2) the cathodic curve corresponding to gallium reduction has moved to a more positive potential, (compared to the position of this wave in 0.1 molar potassium nitrate; see Fig. 5) and its slope has increased greatly; (3) curves in 1.0 and 2.0 molar potassium thiocyanate show a hydrolysis wave which, in each case, is comparable in magnitude to the first cathodic wave. These data indicate that the acid-base equilibria in solutions at concentrations of thiocyanate as high as two molar are essentially the same as those which exist in the presence of potassium nitrate only; (4) the rising portion of the first cathodic wave is distorted. The distortion appeared less pronounced in 1.0 molar thiocyanate, but it is severe at the higher salt concentration. This behavior might result if the polarographic current were controlled by unfavorable electrode kinetics instead of the usual diffusion processes.

The uninflected character of the current as it crosses the zero current axis does not lend support to this idea, however, since this behavior indicates that both the forward and reverse electrode reactions are occurring rapidly and with nearly the same rate.⁷²

More probably, the observed distortion is caused by a "fusing" of two cathodic waves occurring at nearly the same potential. Experimental evidence was subsequently found to support this contention. A detailed discussion of this evidence will be given in a later section. The observations noted under (3) concerning the acid-base equilibria in one and two molar thiocyanate suggest the following equation as a means of explanation:

Thus, the increasing thiocyanate concentration would successively substitute for the bound water molecules without changing the acidity of the solution. The bound hydroxyl ions are very strongly attached.³⁸ Thiocyanate forms relatively weak complexes with metals of this periodic subgroup, and it would be expected, therefore, that a large excess of this ligand would be necessary to displace the already tightly bound hydroxyl group. Partial confirmation of this hypothesis was furnished from later experiments which showed no polarographic hydrolysis wave in solutions containing 0.5 millimolar Ga^{+3} in 7.5 molar potassium thiocyanate.

It would appear that this question could be resolved

using a combination of the glass electrode and silver-silver thiocyanate electrode to test equation (40).

The effect of thiocyanate in improving the character of the gallium reduction wave has already been shown graphically in Figure 8. The data shown in Figure 9 also indicates that gallium reduction characteristics are improved in one molar thiocyanate. It seemed fitting, therefore, to examine the reduction behavior at much higher ligand (SCN) concentrations.

Qualitative, composite polarographic curves which were obtained in nearly saturated (25°C.) potassium thiocyanate solutions, appeared reversible. Because of the experimental uncertainties involved in working with saturated solutions of potassium thiocyanate of such high concentrations (about 25. molar at room temperature¹²⁶),

(126) International Critical Tables Volume 4, p. 241.

a ten molar stock solution was prepared and standardized. When this stock solution was used to prepare polarographic test solutions containing 7.5 molar potassium thiocyanate, the polarographic waves which were obtained were equally as good as those obtained in solutions saturated with potassium thiocyanate.

Thus, it was decided that 7.5 molar represented an "optimum" concentration of potassium thiocyanate which

could be used in subsequent test solutions for the further evaluation of polarographic reversibility. Since the presence of complexing impurities in a solution of such concentration could greatly effect polarographic behavior, reagent grade potassium thiocyanate was subjected to two recrystallizations at 0.0°C. from demineralized, double distilled water, and immediately air dried. Data taken using the purified salt were no different from that obtained with the reagent, "analyzed" grade.

Figure 10 represents corrected data which are typical of that obtained with the gallium amalgam (0.0002% gallium dropping ($m^{2/3}t^{1/6} = 2.143 \text{ mg}^{2/3} \text{ sec.}^{-1/2}$ at -1.00 volt vs. S.C.E.) into a solution 0.0005 molar in gallium nitrate and 7.5 molar in potassium thiocyanate. The addition of a maximum suppressor to the solution was found unnecessary at high concentrations of thiocyanate. It is generally known that polarographic maxima do not occur at the isoelectric point of mercury, hence, because of the strong tendency of SCN^- to adsorb (see Table 1) on the drop surface, thus shifting the isoelectric point, the gallium electrode reaction shown in Figure 10 may actually have taken place in this region of maximum surface tension.

The cathodic limiting current of this wave is half that obtained with the same concentration of gallium in 0.1 molar potassium nitrate. This behavior could be a reflection of the effect of increased solution viscosity

Fig. 10.--Composite Ga wave and residual current curve. Test solution: 5×10^{-4} molar $\text{Ga}(\text{NO}_3)_3$ in 7.5 molar KSCN (Amalgam XII : 0.0002% Ga; $m^{2/3}t^{1/6} = 2.143 \text{ mg}^{2/3}\text{sec.}^{-1/2}$ at -1.00 volts vs. S.C.E.; see appendixes I and III).

on the diffusion coefficient of the reducing species. If the reducing species were a large complex ion with small diffusion coefficient or if the surface of the amalgam drop were partially blocked by adsorbed thiocyanate, the effect would be the same. It is most probably a combination of all three.

The wave shown in Figure 10 was tested for polarographic reversibility using the criteria of equation (20).

A plot was made of E_{applied} vs. $\log \frac{i-i_d}{i_d-i}$ using data taken from the smoothed, corrected curve, since the slope was too large to obtain a sufficient number of experimental points on the rising portion of the wave. These results are shown in Figure 11. The $E_{1/2}$ value, that is the potential at which $\log \frac{i-i_d}{i_d-i} = 0$, is -0.900 ± 0.003 volt vs. S.C.E. The reciprocal slope of the straight line was determined to be 0.020 volt in agreement with the theoretical value of 0.020 volt for a three electron reduction.

Even though the typical data represented by figures 10 and 11 for the composite wave in 7.5 molar thiocyanate fulfill an excellent test for polarographic reversibility, as previously discussed, it is not conclusive.

Anodic.--Figure 12 shows a corrected anodic wave taken with the dropping amalgam (0.0002% gallium; $m^{2/3}t^{1/6} = 2.143 \text{ mg}^{2/3} \text{ sec.}^{-1/2}$ at -1.00 volts vs. S.C.E.) electrode in a

Fig. 11.--Plot of $\log \frac{i-i_{da}}{i_{dc}-i}$ vs. E applied for
data shown in Fig. 10.

Fig. 12.--Anodic Ga wave in 7.5 molar KSCN only
(Amalgam XIII : 0.0002% Ga; $m^{2/3}t^{1/6} = 2.143 \text{ mg sec.}^{-1/2}$
at -1.00 volts vs. S.C.E.; see Appendix IV).

Figure 13 shows a plot of E_{applied} vs. $\log \frac{i-i_{\text{da}}}{i}$ for the anodic wave. At $\log \frac{i-i_{\text{da}}}{i} = 0$, the anodic $E_{1/2}$ value measured -0.906 ± 0.003 volt vs. S.C.E. The reciprocal slope of the resulting straight line was found to be 0.022 volt which is in good agreement with the theoretical value of 0.020 volt for the reversible oxidation to trivalent gallium. The data in Figure 13 deviate slightly from linearity at both ends, but this was attributed to the difficulty of measuring small differences in current strength in these regions of the curve.

Cathodic.--The polarographic behavior of the gallium couple at the dropping mercury electrode ($m^{2/3}t^{1/6} = 2.403 \text{ mg}^{2/3}\text{sec.}^{-1/2}$ at -1.20 volts vs. S.C.E.) is shown by the two corrected cathodic curves of Figure 14.

The two corrected curves, A and B, were obtained 24 hours apart with the same test solution which was composed of 0.0005 molar gallium nitrate in 7.5 molar potassium thiocyanate. Curve A was obtained first. This curve indicates the presence of two waves which occur at -0.900 volt and -1.13 volt vs. S.C.E. Curve B taken 24 hours later shows that the second, drawn out wave has nearly disappeared. It is suggested that this second irreversible wave is caused by a gallium complex ion, possibly a hydroxy or higher thiocyanate - hydroxy species, which is part of a slowly changing equilibrium. The presence of

Fig. 13.--Plot of $\log \frac{i-i_{da}}{i}$ vs. E_{applied}

for data shown in Fig. 12.

Fig. 14.--Cathodic Ga waves of 5×10^{-4} molar $\text{Ga}(\text{NO}_3)_3$ in 7.5 molar KSCN. Curves A and B taken of same solution; Curve B taken 24 hours after Curve A ($m^{2/3}t^{1/6} = 2.403 \text{ mg}^{2/3}\text{sec.}^{-1/2}$ at -1.20 volts vs. S.C.E.; see Appendix II).

this second cathodic wave is significant in that it could account for the distortion of the cathodic gallium wave which was observed at lower thiocyanate concentrations.

By utilizing a polarographic bias circuit to suppress the first cathodic wave, coupled with increased galvanometer sensitivity, this second wave might be further studied to determine what species are present.

Figure 15 shows the logarithmic plot for the gallium reduction of curve A. The $E_{1/2}$ at $\log \frac{i}{i_{dc}-i} = 0$ is -0.899 ± 0.003 volt vs. S.C.E. The reciprocal slope of the straight line, 0.022 volt, agrees with the theoretical value.

Thus far in this discussion, it has been shown that for solutions 7.5 molar in potassium thiocyanate the following conditions hold: (1) The gallium composite wave obeys, within experimental error, equation (20), the general equation for the polarographic wave. Inherent in equation (20) is the condition that the polarographic current should exhibit no inflection when crossing the zero current axis. (2) The anodic composite and cathodic polarographic waves have the same half-wave potential.

An additional criterion of reversibility requires that the half-wave potential be independent of metal ion concentration. Figure 16 shows a typical series of

Fig. 15.--Plot of $\log \frac{1}{i_{dc}-i}$ vs. E_{applied} for
data of Curve A shown in Fig. 14.

Fig. 16.-- $E_{1/2}$ vs. Ga^{+3} in 7.5 molar KSCN.
Ga concentration (millimolar): (a) 0.00, (b) 0.23,
(c) 0.42, (d) 0.58, (e) 0.72, (f) 0.83.

corrected polarographic waves taken with the dropping mercury electrode ($m^{2/3}t^{1/6} = 2.403 \text{ mg}^{2/3}\text{sec.}^{-1/2}$ at -1.20 volts vs. S.C.E.) in 7.5 molar potassium thiocyanate at gallium concentrations varying from 0.0 to 0.83 millimolar Ga^{+3} . Graphical measurement of the half-wave potentials of these curves has shown them all to be -0.900 volt, within an experimental error of ± 0.003 volt. Polarograms taken of solutions containing gallium at higher concentrations, e.g. 2.5 millimolar, exhibited half-wave potentials which were in agreement with those shown in Figure 16.

In summarizing, under the conditions imposed by the preceding experiments, the gallium couple fulfills all the criteria for polarographic reversibility which are inherent in equation (20).

Concentration dependence of limiting current.--The derivation of the Heyrovsky-Ilkovic equation, i.e., equation (20), which has already been discussed under "Theory", is based on a fundamental tenet of the Ilkovic equation: $i_{\text{diffusion}} = kC$. Therefore, should equation (20) be fulfilled, the conditions imposed by the Ilkovic equation are automatically verified. However, as a check, and as an important adjunct to any polarographic study, experiments to determine the variation of the limiting current with the concentration of reacting species are very important.

In this investigation a study of this kind was of special interest from an analytical viewpoint, for it was desirable to know if the polarographic method could successfully detect or determine gallium in dilute solutions. For this experiment the dropping mercury electrode was adjusted and placed in a cell containing only 7.5 molar potassium thiocyanate. A solution containing gallium nitrate dissolved in 7.5 molar potassium thiocyanate was added in previously calculated increments to give increasing, known, nominal concentrations of Ga^{+3} .

Figure 17 shows the results of this experiment. The limiting current varies linearly with gallium concentration, that is, it follows an Ilkovic-type equation down to a value of $3. \times 10^{-4}$ molar gallium, whence it varies non-linearly until it reaches zero at $1. \times 10^{-4}$ molar gallium.

It can be seen that the data do not follow the true Ilkovic equation which specifies that the limiting current must be zero when $C_{\text{Ga}} = 0$. This experiment suggested, however, that the polarographic method holds excellent promise as a means of accurately determining gallium in solutions high in thiocyanate.

Diffusion control.¹²⁷--An experiment was performed to

(127) Kolthoff and Lingane op. cit. Vol. I, Chap. IV.

Fig. 17.-- i_d vs. Ga^{+3} in 7.5 molar KSCN;
 Ga^{+3} ; 0.0 to 1.0 millimolar (data taken at 1.20
volt vs. S.C.E.; $m^{2/3}t^{1/6} = 2.403 \text{ mg}^{2/3} \text{ sec.}^{-1/2}$ at -1.20
volts vs. S.C.E.)

determine whether the limiting current observed at the dropping mercury electrode was controlled by diffusion. It has been shown¹²⁷ that a polarographic current which is controlled entirely by diffusion follows the linear relationship,

$$(41) \quad i_{\text{diffusion}} = k(m^{2/3} t^{1/6}) = k'(h_o^{1/2})$$

where k and k' are constants and h_o is the mercury pressure corrected for solution back pressure: that is, the mercury height, in centimeters, above the capillary orifice.

Figure 18 shows a linear variation of $h_o^{1/2}$ vs. i_{d_o} for the mercury electrode dropping into 0.005 molar gallium nitrate solution which was also 7.5 molar in potassium thiocyanate. The experiment was conducted at an applied potential of -1.20 volts vs. S.C.E. (25°C.)

It was thus concluded that under these conditions the polarographic limiting current was diffusion controlled.

Effect of acidity on gallium polarography.--Zittel⁴² and others¹²⁸ have already shown that lowering the pH of

(128) J. Szonntag and J. Rozmanith, Acta Chim. Acad. Sci. Hungary, 9, 99 (1956).

Fig. 18.-- i_{d_0} vs. $h_0^{1/2}$; test solution: 5×10^{-3}
molar $\text{Ga}(\text{NO}_3)_3$ in 7.5 molar KSCN.

a gallium nitrate solution increases the height of its polarographic reduction wave. Zittel found that the limiting current increased at a decreasing rate until it became constant at $\frac{H^+}{Ga^{+3}} = 50$. This behavior apparently is caused by a reversal of the hydrolytic equilibrium,

It was found in this investigation that increasing the acidity, even slightly, of a test solution which was 7.5 molar in potassium thiocyanate caused an increase in cathodic diffusion current coupled with a deterioration in the shape of the wave. An increase in acidity of the solution subsequently caused a yellow solid to precipitate which was thought to be thiocyanagen or polymerized thiocyanic acid.

The general deterioration in the shape of the reduction wave in 7.5 molar potassium thiocyanate as the acidity is increased indicates that the species giving reversible reduction behavior may be comprised of mixed hydroxy-thiocyanate ions. Thus, as the (H^+) increases, the hydroxy anion would be displaced from the structure of the electroactive ion yielding either a "pure" thiocyanate complex or an aquo-thiocyanate complex which is "less reversibly" reduced than the mixed hydroxy-thiocyanate ion.

CHAPTER VII

DISCUSSION OF RESULTS - II INDIUM

Polarography of indium.--As discussed in the introduction to this work the electrochemistry of indium, particularly the polarography of indium, is well known and has been better defined, generally, than that of gallium.

The study of indium polarography in this investigation was intended to give comparison with the gallium work in three aspects: (1) polarographic reversibility; (2) polarographic measurement of hydrolysis; (3) effect of increasing thiocyanate concentration on the shape and half-wave potential of the indium reduction wave.

Lingane⁸⁶ has found that the polarographic reduction of the aquo indic ion in perchloric acid is irreversible. This has been confirmed in nitrate and perchlorate solutions by Bulovova.⁵⁵ Lingane found, however, that gradual addition of either Cl^- or I^- to the solution moved the irreversible indium wave ($E_{1/2} = -0.95$ volt vs. S.C.E.) to more positive (less reducing) potentials. His study showed that the wave was reversible in 0.1 molar and 1.0 molar potassium chloride with $E_{1/2}$ values of -0.561 and -0.597 volt vs. S.C.E. respectively.

Schufle⁵⁴ et al. in their study of the chloro-indium complexes could not confirm the work of Lingane or Bulovova for the irreversible reduction of In^{+3} in perchlorate.

Instead, they found that 0.001 molar indium perchlorate in 0.1 molar perchloric acid gave a reduction wave whose logarithm plot was a straight line. The half-wave potential obtained from this plot was given as -0.573 volt vs. S.C.E. at $25^{\circ}\text{C}.$; the slope of this plot indicated that the reduction reaction was occurring with a change of 2.8 electrons, which is in good agreement with the theoretical 3 electron change.

Figure 19 shows a plot of polarographic data corrected for residual current taken of 0.5 millimole indium chloride in 0.1 molar potassium nitrate containing 0.005% gelatin. Two cathodic waves are evident. The first, having an $E_{1/2}$ of -0.521 volt vs. S.C.E., represents the reduction of In^{+3} to the metal, while the second, at $E_{1/2} = 1.48$ volts vs. S.C.E., corresponds to the reduction of hydrogen ion produced by the hydrolysis of the trivalent indium ion. This latter potential is within 20. millivolts of being identical with the half-wave potential (-1.50 volts vs. S.C.E.) obtained for gallium hydrolysis (see Fig. 5). This variation in $E_{1/2}$ value may be accounted for in part by a difference in the standard reduction potential of the calomel electrode (including the junction potentials), which on checking was found to be 10 millivolts less positive (less oxidizing) than when the cell was used for the gallium work.

It will be noted in Figure 19 that the trivalent

Fig. 19.--Cathodic wave of InCl_3 showing associated hydrolysis wave. Test solution: 5×10^{-4} molar InCl_3 in 0.1 molar KNO_3 containing 0.01% gelatin.

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indium reduction wave is very well defined, and, in fact, a plot of E_{applied} vs. $\log \frac{1}{i_d - i}$ for this wave is a straight line with a reciprocal slope of 0.022 volt, in good agreement with the theoretical value of 0.020 volt for a three electron reduction.

The log plot for the wave shown in Figure 19 is given in Figure 20 where it is seen that the experimentally measured $E_{1/2}$ value equals -0.521 volt vs. S.C.E. (25°C.). When this half-wave potential is corrected for the 10 millivolt difference in the measured value of the reference electrode it becomes -0.531 volt vs. S.C.E. It will be remembered that this potential refers to the reduction of 0.5 millimolar In^{+3} in the presence of "equivalent" chloride, i.e., 1.5 millimolar Cl^- .

Although the chloro complexes of In^{+3} are rather "weak",¹²⁵ still, even in equivalent chloride a significant amount of the total indium present would be bound up in the form of cationic chloro complexes ($\log k_{f1}=2.36$), e.g., InCl^{+2} and InCl_2^{+1} .¹²⁹ According to the Heyrovsky-

(129) D. Cozzi and S. Vivarelli, Z. Elektrochem., 57, 408 (1953); 58, 907 (1954).

Ilkovic equation modified for complexing cations, the $E_{1/2}$ value for the simple, uncomplexed In^{+3} ion would

Fig. 20.--Plot of $\log \frac{i}{i_{dc}-i}$ vs. E_{applied}
for data shown in Fig. 19.

be shifted to slightly more negative values should such complexing occur. Thus, the observed $E_{1/2}$ value, -0.531 volt, probably represents a potential which is slightly more negative (more reducing) than that corresponding to the simple ion, In^{+3} , and is considerably more positive, as would be expected, than -0.561 or -0.597 volt reported by Lingane for 0.1 and 1.0 molar potassium chloride solutions respectively.

In the light of these experimental observations it is very difficult to reconcile the findings of Schufle et al. Their value of -0.573 volt vs. S.C.E. appears unreal. This unusually negative value might easily have been observed if (1) observed potentials were not corrected for the IR drop in the solution; (2) the potential of the reference electrode, including junction potentials, was not measured accurately; (3) complexing material occurred in the perchlorate media; or (4) the presence of some irreversibility occurred in the wave, although this appears to have been ruled out owing to the fact that the reported data fitted equation (20), the Heyrovsky-Ilkovic equation. Equation (20) indicates that metals forming amalgams with mercury will often exhibit a polarographic half-wave potential which is nearly the same as the standard electrode potential for that metal.¹³⁰ Indium might

(130 Kolthoff and Lingane op. cit. Vol. I, p. 198 table XI-2.

be expected to behave similarly. Latimer¹³¹ lists the

(131) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., N. Y. 1952, p. 158.

standard oxidation potential for indium which was obtained by Hattox and DeVries¹³² for the metal in contact with

(132) E. M. Hattox and T. DeVries, J. Am. Chem. Soc., 58, 2126 (1936).

sulfate solutions. Their value of +0.342 volt vs. N.H.E. converts to -0.584 volt vs. S.C.E. If this potential is comparable in magnitude to the $E_{1/2}$ value for the polarographic wave in sulfate solution, some complexing evidently is occurring.

Hence, it would appear that the reversible $E_{1/2}$ value of indium (-0.531 volt vs. S.C.E.) obtained for equivalent chloride may well represent a close approximation to the uncomplexed, standard potential of this couple. When compared to the Normal Hydrogen Electrode this becomes, assuming that the S.C.E. = +0.242 volt at 25°C. vs. N.H.E., +0.289 volt vs. N.H.E. for the oxidation.

Figure 21 shows the polarographic behavior of the indium couple in the presence of an increasing concentration of thiocyanate ion. The solution consisted initially

Fig. 21.-- $E_{1/2}$ vs. KSCN : Cathodic In wave
(initial test solution: 5×10^{-4} molar InCl_3 in
 KNO_3); KSCN (moles/liter): (1) 0.00, (2) 0.05,
(3) 0.10, (4) 0.15, (5) 0.20, (6) 0.25, (7) 0.30,
(8) 0.35, (9) 0.40, (10) 0.45, (11) 0.50.

of 0.5 millimolar indium chloride in 2.0 molar potassium nitrate containing 0.005% gelatin. The potassium thiocyanate was prepared from a 10.0 molar stock solution.

It is immediately evident from these curves that the presence of even a small quantity of thiocyanate has a significant effect in shifting the indium half-wave potential to more negative values.

To determine the true effect of thiocyanate on the indium wave it was necessary to observe the indium reduction in noncomplexing (i.e., NO_3^-) media, since the data shown in Figure 21 were obtained in solutions containing chloride. The nitrate salt of indium was not readily available for this purpose, hence it was decided to prepare a 0.01 molar solution of indium nitrate directly from the "specpure" metal. Enough boiled, concentrated reagent nitric acid was used to dissolve the indium metal and to suppress any resulting hydrolysis. With the calculated excess of nitric acid the following reaction was presumed to occur:

The added excess nitric acid was such that when the dissolved indium was made up to 250 ml. the $\text{H}^+ = 1.0$ molar

$\frac{\text{H}^+}{\text{In}^{+3}} = 100$. This stock solution was used subsequently

to prepare polarographic test solutions.

A test solution composed of 0.5 millimolar indium nitrate in 2.0 molar potassium nitrate containing 0.005% gelatin and having a measured pH of 1.20 showed no indium reduction wave at the dropping mercury electrode. In the belief that the irreversible indium wave may have been shifted behind the hydrogen wave at this high ionic strength,^{43,70} the data were repeated in a solution which was at a pH of 1.35 and 0.1 molar in potassium nitrate. Again no reduction wave was observed. It was concluded that the low pH of these test solutions resulted in a hydrogen wave which coincided with the irreversible indium wave which Lingane¹³³ has shown to have an $E_{1/2}$

(133) Kolthoff and Lingane op. cit. p. 519.

value of -0.95 volt vs. S.C.E. in perchlorate solutions.

The four curves shown in Figure 22 illustrate qualitatively the effect of adding potassium thiocyanate to the indium nitrate test solution. In the presence of 0.1 molar thiocyanate the wave has shifted to a more positive value and has become very well defined. Reduction waves obtained in 0.2, 0.3 and 0.4 molar potassium thiocyanate show a regular shift to more negative values indicating strongly that complex formation is occurring between In^{+3} and SCN^- .

In this connection it is interesting to note that

Fig. 22.-- $E_{1/2}$ vs. KSCN : Cathodic In waves
(initial test solution: 5×10^{-4} molar $\text{In}(\text{NO}_3)_3$ in
 KNO_3); KSCN (moles/liter): (1) 0.10, (2) 0.20, (3)
0.30, (4) 0.40.

only one investigation¹³⁴ has so far been reported on the

(134) N. Sunden, Svensk. kem. Tidskr., 66, 20
(1954).

determination of the $\text{In}^{+3} - \text{SCN}^-$ complexity constants. No polarographic determination of these constants has yet been reported.

To understand the polarography of indium more fully and to provide a wider base for its comparison with that of gallium, it was decided to fabricate a dropping indium amalgam electrode. Some qualitative results have already been reported by Bulovova⁵⁵ for the dropping indium amalgam.

A 0.0005% indium amalgam was prepared and used in a way already described for gallium. In operation it was found necessary to exclude oxygen from the system, as the indium amalgam exhibited a strong affinity for this element.

Figure 23 shows a composite polarographic wave which was obtained with the indium amalgam (0.0005% indium dropping into a solution composed of 1.0 millimolar indium nitrate in 0.1 molar potassium thiocyanate containing 0.01% freshly prepared gelatin. The wave shown in Figure 23 was obtained with the Leeds Northrup automatic recording Electrochemograph just prior to taking the same data with the manual instrument. The null potential (approximate

Fig. 23.--Automatically recorded composite wave of In^{+3} in the presence of 0.1 molar KSCN. (indium amalgam : 0.0005% In).

$E_{1/2}$) for this wave was -0.555 volt vs. S.C.E. (measured with the manual instrument). It can be seen from these data that the anodic indium wave is well-defined and that the polarographic current crosses the zero current axis with no inflection, indicating that the reaction is occurring reversibly. The cathodic portion of the wave is very well-defined until the potential reaches a value about 0.25 volt more negative than the $E_{1/2}$, at which point the limiting current decreases to a minimum then begins to rise in a manner completely analogous to that found by Lingane⁸⁶ for indium chloride solutions.

An attempt to obtain a composite wave for a solution containing 1.0 millimolar indium nitrate in 0.2 molar potassium nitrate containing 0.1% freshly prepared gelatin gave a well-defined anodic wave whose $E_{1/2}$ was -0.47 volt vs. S.C.E. This potential is considerably more positive (less reducing) than that which would be expected for a reversible anodic oxidation (c.f. to the $E_{1/2}$ value of the reduction wave in equivalent chloride) in this solution. More significant, perhaps, was the observation that almost no cathodic current was obtained. This is in agreement with the previously discussed observations, which were obtained with indium nitrate at the dropping mercury electrode.

It thus appears that indium, like gallium, is irreversibly reduced at the dropping electrode in nitrate media.

Further, it was evident that the presence of thiocyanate, like chloride, has a very pronounced effect on the character of indium reduction at the dropping electrode. Its enhancing effect is significantly greater in the reduction of indium than in the corresponding process for gallium, where it was found that concentrations of thiocyanate as high as 7.5 molar were necessary before the wave exhibited reversibility.

While examining the polarography of indium at the dropping mercury electrode and at the dropping indium amalgam electrode, perhaps the most noted aspect was the "minimum" in the diffusion current plateau. This was first observed by Lingane⁸⁶ for indium chloride solutions containing an excess of potassium chloride. The minimum was also observed in this investigation in the presence of potassium thiocyanate. However, the minimum was not observed in a nitrate solution containing indium with equivalent chloride (see Fig. 19).

Lingane noted that the low point of the minimum occurred near -1.4 volts vs S.C.E. It was found in this work that the addition of sufficient Triton X-100 to a solution of indium containing equivalent chloride caused the cathodic diffusion current to disappear. When the potential of the electrode, however, was increased to -1.4 volts vs S.C.E., the current rose again to the diffusion

value before the final current rise corresponding to hydrogen reduction.

This phenomenon does not appear to be confined to the polarography of indium. In 1950, Laitinen and Onstott¹³⁵ reported observing similar behavior in the

(135) H. A. Laitinen and E. E. Onstott, J. Am. Chem. Soc., 72, 4565 (1950).

polarography of the chloroplatinate ion, PtCl_6^- . They found that, in the absence of camphor, a reduction wave occurred which began at 0.00 volt vs. S.C.E. At more negative potentials the cathodic diffusion current was observed to decrease, reach a minimum at -1.4 volts vs. S.C.E., then rise to its previous value. In the presence of camphor, however, no cathodic wave was noted until a potential of -1.35 to -1.40 volts was reached. Laitinen and Onstott postulated that, in the absence of camphor, PtCl_6^- may be reduced by either of two mechanisms: (1) "ordinary" irreversible reduction with $E_{1/2} = -1.35$ volts vs. S.C.E., or (2) reduction at more positive potentials through the mechanism of the adsorption of PtCl_6^- at the drop surface. They further postulate that at high negative potentials the PtCl_6^- is desorbed, and the current falls to a low magnitude until the potential has reached a high enough negative value at which point

the alternative, irreversible process occurs, hence, the current rises to its previous value. This phenomenon appears entirely comparable to that observed in this work for indium reduction in chloride and thiocyanate. Further, the presence of Triton X-100 has an effect on the indium reduction which is directly analogous to that of camphor in the reduction of chloroplatinate ion.

Laitinen and Onstott¹³⁵ have developed a series of equations which describe the reversible desorption at an electrode surface of an adsorbed species (e.g. camphor), and which, in addition, define a "half-wave" potential for the reversible desorption process.

These phenomena are most interesting, and it would appear from the literature that further investigative work should be undertaken.

CHAPTER VIII

RESULTS AND DISCUSSION: III

HYDROLYSIS OF Ga AND In

Although a study of the hydrolysis of Ga^{+3} and In^{+3} was not a part of this investigation, the presence of polarographic hydrolysis waves on the normal reduction curves of these metals permitted an approximation to be made of their first hydrolysis constants. A brief discussion of the calculation of these constants and their comparison with those in the literature appears worthwhile at this point.

Calculation.--The calculation of the following hydrolysis constants assumes that the trivalent metal-ion hydrolyses according to the following, one step reaction:

As already discussed, the trivalent gallium and indium ions are quite acidic. The Ga^{+3} appears to be the stronger acid. For this reason equation (42) is only an approximation of the total hydrolytic equilibrium, which undoubtedly involves some $\text{Ga}(\text{OH})_2^+$.

The hydrolysis constant, K_{hyd} , was calculated on the basis of the following assumptions: (1) the height, a , of the corrected polarographic hydrolysis wave is proportional to the hydrogen ion concentration contributed by

the reaction in equation (42), (2) the height, b , of the corrected metal reduction wave is proportional to the equilibrium, "free" metal concentration, (3) the sum, $(a+b)$ of the two corrected heights is proportional to the total, nominal concentration of dissolved metal salt, C_{salt} .

The Mass Action Law applied to equation (42) gives

$$(43) \quad K_{\text{hyd.}} = \frac{M(\text{OH})^{+2} (H^+)}{M^{+3}}$$

$$\text{From equation (42), } M(\text{OH})^{+2} = (H^+)$$

then,

$$(44) \quad K_{\text{hyd.}} = \frac{(H^+)^2}{(M^{+3})} \quad \text{or,}$$

from the foregoing discussion,

$$(45) \quad K_{\text{hyd.}} = \frac{A^2}{B}$$

where

$$A = \frac{a}{a+b} \times C_{\text{salt}}$$

$$B = \frac{b}{a+b} \times C_{\text{salt}}$$

Gallium.--The polarographic data which were used to calculate the first hydrolysis constant, $K_{\text{hyd.}}$, of tri-valent gallium were obtained with the gallium amalgam (0.0002% gallium: amalgam XII) dropping into a solution which was 0.5 millimolar in gallium nitrate, 0.1 molar in potassium nitrate and contained 0.005% freshly prepared

gelatin. These data are identical to those shown in Figure 5 except for the cathodic diffusion currents which were corrected for the residual current.

The gallium hydrolysis constant calculated by this method is listed in Table 8 where it is compared with the results reported by other investigators.^{11,12,38,125,136,137}

(136) R. Fricke and K. Meyring, Z. Anorg. Chem., 176, 325 (1928).

(137) A. S. Wilson and H. Taube, J. Am. Chem. Soc., 74, 1355 (1952).

Indium.--The polarographic data which were used for the calculation of the first indium hydrolysis constant were obtained with the dropping mercury electrode. The test solution was composed of 0.5 millimolar indium chloride in 0.1 molar potassium chloride which was 0.005% in freshly prepared gelatin. The data, corrected for residual current, were taken directly from those shown in Figure 19. Table 8 compares the values obtained by previous investigators^{132,138,139,140} with the constant calculated

(138) T. Moeller, J. Am. Chem. Soc., 63, 1206 (1941).

(139) G. Biederman, Arkiv. Kemi, 9, 277 (1956).

(140) F. J. C. Rossotti and H. Rossotti, Acta Chim. Scand., 10, 779 (1956).

using the results obtained in this investigation.

Table 8

Comparison of Ga, In Hydrolysis Constants

Element	log K ₁	Method of Measurement	Solution	Reference
Ga	-2.8	H ₂ (pt)	Corrected to inf. dil.	136
	-3.3	Polarographic hydrolysis wave	0.1 M KCl	12
	-3.3 to -3.43	Glass electrode	Variable	11
	-2.92	Spectrophotometry	Ionic strength adjusted to 0.5 with NaClO ₄	137
In	-3.70	Quinhydrone		132
	-4.92	Glass electrode	InCl ₃ :varied	138
	-3.85		Varied	
	-4.42	In-Hg, glass	3. M NaClO ₄	139
	-4.4	Distribution	3. M NaClO ₄	140
Ga ^a	-3.4	Pol. hydrolysis wave	Ga(NO ₃) ₃ in 0.1 M KNO ₃	
In ^b	-4.5	"	InCl ₃ in 0.1 M KNO ₃	

a: $i_{d_{Ga+3}} = 4.0$ micro amp. (-1.3 volts vs. S.C.E.); $i_{d_{H+}} = 5.3$ micro amps (-1.60 volts vs. S.C.E.) b: $i_{d_{In+3}} = 4.70$ micro amps. (-0.60 volt vs. S.C.E.); $i_{d_{H+}} = 1.30$ micro amps. (-1.60 volts vs. S.C.E.).

CHAPTER IX

SUMMARY AND CONCLUSIONS

1. A unique experimental procedure has been developed for the preparation and use of a dilute dropping gallium amalgam electrode. This procedure was shown to be convenient also when using the dropping indium amalgam.

It has been shown experimentally that the gallium and indium in these amalgams have a great tendency to oxidize. Further, the amalgams remained stable toward oxidation only if air and moisture were rigidly excluded from the apparatus. Tygon tubing was found inadequate for containing the amalgam. It was concluded that some property of the Tygon, perhaps its affinity or permeability for oxygen, was responsible for this behavior. An all-glass apparatus was designed for stabilizing and holding the amalgam after preparation.

2. Experiment has shown that well-defined anodic polarographic waves as well as cathodic waves may be obtained in potassium nitrate solutions containing gallium. An irreversible, cathodic hydrolysis wave is also obtained in this medium. These cathodic waves, although irreversible, agreed well, as to $E_{1/2}$ and i_d , with those obtained by Challenger in his study using the dropping mercury electrode. The results obtained in this medium also agreed with those obtained by Zittel in potassium nitrate. It was concluded from this study, which confirmed the work

of prior investigators, that gallium may be polarographically determined in potassium nitrate if its concentration is less than about 1 millimolar. Gelatin, at concentrations less than 0.01%, was used successfully as a maximum suppressor in potassium nitrate.

Anodic and cathodic waves which were obtained in potassium nitrate indicated that the overpotential, that is, ($E_{1/2 \text{ anodic}} - E_{1/2 \text{ cathodic}}$), for the gallium reaction was 0.29 volt.

Further, the measured anodic half-wave potential of a 0.0002% amalgam falls in the range of potentials predicted by the Nernst equation.

3. As previously discussed, the presence of fluoride, chloride, bromide, iodide, perchlorate, sulfate, nitrate, formate, acetate, malonate, oxalate, citrate, phthalate, E.D.T.A. and sulfosalicylic acid have no improving effect on the gallium wave at the dropping mercury (amalgam) electrode. Experimental observation, however, has confirmed the salutary effect of salicylate and thiocyanate on the gallium wave.

4. The study was extended to an investigation of gallium polarography in potassium thiocyanate as supporting electrolyte. Investigations at both the dropping mercury and dropping amalgam electrodes indicated an improvement in the shape of the gallium wave on increasing the thiocyanate concentration. The investigation was

therefore carried to higher thiocyanate concentrations, the effect of which was to improve the slope of the composite and cathodic waves of gallium while simultaneously shifting the $E_{1/2}$ to more negative values vs. S.C.E. Potassium thiocyanate at 7.5 molar was adopted as an "optimum" concentration for further study.

At this concentration, the anodic, composite and cathodic waves satisfied the criteria inherent in the Heyrovsky-Ilkovic equation as to polarographic reversibility. It was therefore concluded that, under these conditions, gallium reacts reversibly at the dropping mercury (amalgam) electrode.

Further, it was noted that maximum suppressors were unnecessary when data were taken in 7.5 molar potassium thiocyanate. This was attributed to a shift in the isoelectric point of mercury to more negative values.

5. In 7.5 molar potassium thiocyanate gallium reduction at the dropping electrode is governed by diffusion.

6. The variation of the diffusion current with the concentration of gallium, in the presence of thiocyanate, resulted in a linear relationship from about 1 millimolar Ga^{+3} down to 0.3 millimolar. Below 0.3 millimolar gallium, the current decreased non-linearly until it reached zero at about 0.1 millimolar. It was thus concluded that the polarographic method might be used in solutions high in thiocyanate to accurately determine Ga^{+3} above about 0.3 millimolar.

7. Further study of gallium at the dropping mercury electrode has shown (in thiocyanate solutions) the presence of a time dependent, irreversible wave occurring at a point (-1.13 volts vs. S.C.E.) just following the gallium reduction wave. It is postulated that this polarographic wave may be attributed to a reducible gallium species which occurs as part of a slowly changing equilibrium.

8. It has already been mentioned that no good, direct electroanalytical method exists for the determination of gallium, principally because of its irreversible behavior in electrochemical reactions.

It would appear from the results of this investigation that amperometric, coulometric, potentiometric, polarographic and controlled potential deposition may be used as methods for its electroanalytical determination.

9. This investigation has shown that the electroreduction of In^{+3} at the dropping electrode is very strongly affected (in contrast to Ga^{+3}) by the presence of small concentrations of thiocyanate. A minimum was noted at -1.1 volts vs. S.C.E. on the diffusion current plateau in the presence of thiocyanate.

Contrary to Lingane's observations in 1. and 0.1 molar potassium chloride, the reversible indium wave showed no minimum in equivalent chloride.

10. A $E_{1/2}$ potential of -0.531 volt vs. S.C.E. at 25°C. was measured for the reversible indium wave in equivalent chloride. A recently reported investigation has indicated that the $E_{1/2}$ value for the simple, uncomplexed In^{+3} reduction wave is -0.573 volt vs. S.C.E. This potential conflicts directly with the results obtained in this investigation and suggests that a redetermination of the standard potential of the indium couple should be undertaken.

A P P E N D I X E S

APPENDIX I

Figure 10

Residual Curve : Hg Electrode

(Run #84A)

7.5 molar KSCN,
 $h_{\text{Hg}} = 73.8 \pm 0.1$ cm. $t = 3.4$ sec. at -1.2 volts vs. S.C.E. $T = 25.0 \pm 0.1^\circ\text{C}.$

<u>E vs. S.C.E.</u> <u>(measured)</u>	<u>i</u> <u>(microamperes)</u>
-0.401	-0.78
-0.420	-0.43
-0.441	-0.24
-0.461	-0.14
-0.481	-0.10
-0.500	-0.07
-0.542	-0.04
-0.562	-0.02
-0.600	-0.01
-0.620	-0.00
-0.640	+0.01
-0.660	+0.02
-0.700	+0.04
-0.800	+0.09
-0.901	+0.20
-0.999	+0.17
-1.099	+0.21
-1.199	+0.25
-1.299	+0.30
-1.398	+0.34
-1.498	+0.41
-1.596	+0.74

APPENDIX II

Figure 14

Cathodic Wave : Hg Electrode

(Run #85)

0.5 millimolar $\text{Ga}(\text{NO}_3)_3$

7.5 molar KSCN

 $t = 3.4$ sec. at -1.2 volts vs. S.C.E. $h_{\text{Hg}} = 73.7 \pm 0.1$ cm. $T = 25.0 \pm 0.1^\circ\text{C}.$

<u>E vs. S.C.E.</u> <u>(measured)</u>	<u>E vs. S.C.E.</u> <u>(IR corrected)</u>	<u>i</u> <u>(microamperes)</u>
-0.60090	-0.6009	0.00
-0.6469	-0.6417	+0.01
-0.70161	-0.7016	+0.04
-0.74565	-0.7456	+0.08
-0.80190	-0.8019	+0.10
-0.82116	-0.8211	+0.11
-0.86211	-0.8621	+0.16
-0.88204	-0.8819	+0.41
-0.90184	-0.9013	+1.27
-0.92185	-0.9211	+1.96
-0.94521	-0.9444	+2.16
-0.96535	-0.9645	+2.24
-0.98816	-0.9873	+2.32
-1.00116	-1.0003	+2.32
-1.01990	-1.0190	+2.36
-1.06094	-1.0600	+2.45
-1.10110	-1.1001	+2.50
-1.20075	-1.1997	+2.66
-1.30164	-1.3004	+2.86
-1.40094	-1.3994	+2.96
-1.50126	-1.5001	+3.03
-1.60049	-1.5991	+3.58

APPENDIX III

Figure 10

Composite Wave : Amalgam XII

(Run #88)

0.5 millimolar $\text{Ga}(\text{NO}_3)_3$

7.5 molar KSCN

 $t = 3.66$ sec. at -0.6 volts vs. S.C.E. $h_{\text{Hg}} = 64.2 \pm 0.1$ cm. $T = 25.0 \pm 0.1^\circ\text{C}.$

<u>E vs. S.C.E.</u> <u>(measured)</u>	<u>E vs. S.C.E.</u> <u>(IR corrected)</u>	<u>i</u> <u>(microamperes)</u>
-0.40085	-0.4027	-4.74
-0.50042	-0.5022	-4.56
-0.60142	-0.6032	-4.54
-0.70096	-0.7027	-4.47
-0.80108	-0.8029	-4.39
-0.84080	-0.8425	-4.30
-0.86063	-0.8619	-4.21
-0.88035	-0.8816	-3.30
-0.90000	-0.9003	-0.661
-0.91913	-0.9186	+1.28
-0.94557	-0.9449	+1.84
-0.96506	-0.9643	+1.93
-0.98455	-0.9838	+1.99
-0.99690	-0.9961	+1.99
-1.01826	-1.0175	+2.04
-1.03976	-1.0390	+2.05
-1.06120	-1.0604	+2.10
-1.08070	-1.0800	+2.12
-1.10114	-1.1003	+2.15
-1.14573	-1.1449	+2.21
-1.18880	-1.1880	+2.24
-1.20239	-1.2015	+2.23
-1.30321	-1.3023	+2.31
-1.40160	-1.4007	+2.38
-1.50173	-1.5008	+2.50
-1.60144	-1.6004	+2.80

APPENDIX IV

Figure 12

Anodic Wave : Amalgam

(Run #91)

0.5 millimolar $\text{Ga}(\text{NO}_3)_3$

7.5 molar KSCN

 $h_{\text{Hg}} = 64.2 \pm 0.1 \text{ cm.}$ $t = 3.77 \text{ sec. } -0.6 \text{ volt vs. S.C.E.}$ $T = 25.0 \pm 0.1^\circ\text{C.}$

<u>E vs. S.C.E.</u> <u>(measured)</u>	<u>E vs. S.C.E.</u> <u>(IR corrected)</u>	<u>i</u> <u>(microamperes)</u>
-0.40085	-0.4028	-4.28
-0.50150	-0.5034	-4.12
-0.60125	-0.6031	-4.08
-0.70192	-0.7037	-4.04
-0.80119	-0.8030	-3.98
-0.82050	-0.8223	-3.94
-0.94153	-0.8433	-3.89
-0.86147	-0.8632	-3.82
-0.88182	-0.8834	-3.39
-0.90176	-0.9027	-2.05
-0.92170	-0.9220	-0.69(6)
-0.94318	-0.9433	-0.15(2)
-0.96325	-0.9635	+0.023(4)
-0.98596	-0.98596	+0.078

APPENDIX V

Spectroscopic Analysis (Johnson Matthey Co., Ltd.)

Gallium Nitrate

Element present	Parts per million	Laboratory No.	Catalog No.
Lead	4		
Boron)			
Copper)	1		
Sodium)		4258	J.M. 367
Aluminum)			
Magnesium)	1		
Manganese)			
Silver)			

Elements sought but not detected: As, Au, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Fe, Ge, Hf, Hg, In, Ir, K, Li, Mo, Nb, Ni, Os, P, Pd, Pt, Rb, Re, Rb, Ru, Sb, Se, Si, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

Indium Chloride

Element present	Parts per million	Laboratory No.	Catalog No.
Calcium	3		
Magnesium	1		
Iron	0.5	10123	J.M. 386
Copper)			
Silver)	0.5		
Sodium)			

Elements sought but not detected: Al, As, Au, B, Ba, Be, Bi, Cd, Co, Cr, Ga, Ge, Hg, Ir, K, Li, Mn, Mo, Ng, Ni, Os, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sb, Si, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

APPENDIX V (continued)

Indium Wire (1.6 mm. diameter)

Element present	Parts per million	Laboratory No.	Catalog No.
Cadmium	1		
Sodium	1		
Aluminum)		8354	J.M. 380
Calcium)			
Lead)	1		
Magnesium)			

Elements sought but not detected: Ag, As, Au, B, Ba, Be, Bi, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, Ir, K, Li, Mn, Mo, Nb, Ni, Os, P, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Si, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

Gallium Metal

Element present	Parts per million	Laboratory No.	Catalog No.
Lead	3		
Calcium)			
Silver)	2	1875	J.M. 360
Copper)			
Magnesium)	1		
Silicon)			

Elements sought but not detected: Al, As, Au, B, Ba, Be, Bi, Cd, Co, Cr, Cs, Fe, Ge, Hf, Hg, In, Ir, K, Li, Mn, Mo, Na, Nb, Ni, Os, P, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

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AUTOBIOGRAPHY

I, Edward Darrell Moorhead, was born in Massillon, Ohio, May 9, 1930. While I was still quite young, my family moved to Canton, Ohio, and it was there that I began my elementary education. Upon returning to Massillon several years later, I completed my secondary education in the public schools of that city, graduating from Washington Senior High School in June 1948. I began studies at the College of Wooster in the fall of the same year. I resumed my studies as a sophomore at the College of Wooster in the fall of 1951, and in 1952 transferred to The Ohio State University, where I began a major in chemistry.

In December of 1954 I obtained the Bachelor of Science degree in Chemistry from The Ohio State University.

I entered the Graduate School of The Ohio State University in January 1955, where I held a graduate teaching assistantship until September 1957. During the 1957-1958 academic year I held a University research fellowship. In September of 1958 I was appointed as assistant instructor, and from January 1959 until my graduation in August I taught sophomore courses in quantitative chemical analysis.