

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THE STANDARD POTENTIAL OF THE COBALT AMALGAM  
AND ACTIVITY COEFFICIENTS OF AQUEOUS  
SOLUTIONS OF COBALT SULFATE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

ERNEST STURCH, JR.

Norman, Oklahoma

1956

THE STANDARD POTENTIAL OF THE COBALT AMALGAM  
AND ACTIVITY COEFFICIENTS OF AQUEOUS  
SOLUTIONS OF COBALT SULFATE

APPROVED BY

*Bernard O. Heston*

*J. C. Colbert*

*J. H. Wender*

*Bruce Houston*

*J. Ross Nelson*

DISSERTATION COMMITTEE

To my wife, Doris Ann

## ACKNOWLEDGEMENT

This work has been carried out under the direction of Dr. B. O. Heston. His patience, guidance and the many helpful suggestions during the course of the research and the writing of the dissertation gave incentive and encouragement to the author.

I am deeply grateful for the interest and assistance of the members of the Department of Chemistry and fellow graduate students; special assistance was given by Dr. P. L. Pickard, Mr. C. L. Dulaney, Mr. R. J. Sonnefeld, Mr. G. W. Polly and Mr. John Anderson.

TABLE OF CONTENTS

	Page
LIST OF TABLES . . . . .	vi
LIST OF ILLUSTRATIONS. . . . .	vii
Chapter	
I. INTRODUCTION. . . . .	1
II. EXPERIMENTAL. . . . .	7
Apparatus and Measuring Setup	
Materials and Solutions	
Experimental Procedures	
Experimental Results	
III. TREATMENT OF DATA AND RESULTS . . . . .	24
IV. DISCUSSION OF METHODS AND RESULTS . . . . .	31
The Experimental Method	
The Amalgam	
The Standard Potential	
The Activity Coefficient	
V. SUMMARY AND CONCLUSIONS. . . . .	38

## LIST OF TABLES

Table	Page
I. Amalgam Potential of 0.0912 Molal $\text{CoSO}_4$ . . . . .	15
II. Amalgam Potentials of 0.230, 0.183, 0.137 and 0.0822 Molal $\text{CoSO}_4$ . . . . .	17
III. Amalgam Potentials of 0.0728, 0.0637, 0.0546 and 0.0456 Molal $\text{CoSO}_4$ . . . . .	18
IV. Amalgam Potentials of 0.0364, 0.0274, 0.0182 and 0.00915 Molal $\text{CoSO}_4$ . . . . .	19
V. Amalgam Potentials of 0.00825, 0.00735, 0.00645 and 0.00556 Molal $\text{CoSO}_4$ . . . . .	20
VI. Amalgam Potentials of 0.00469, 0.00293 and 0.00123 Molal $\text{CoSO}_4$ . . . . .	21
VII. Extrapolation Data and Calculated Activity Coefficients. . . . .	30

LIST OF ILLUSTRATIONS

Figure	Page
1. Basic Wiring Diagram. . . . .	8
2. The Electrolytic Cell . . . . .	10
3. Initial Extrapolation For $E^{\circ}$ . . . . .	28
4. Final Extrapolation For $E^{\circ}$ . . . . .	29
5. Comparison of the Activity Coefficients . . . . .	37

THE STANDARD POTENTIAL OF THE COBALT AMALGAM  
AND ACTIVITY COEFFICIENTS OF AQUEOUS  
SOLUTIONS OF COBALT SULFATE

CHAPTER I

INTRODUCTION

The behavior of electrolytic solutions involves basically the activity of the electrolyte which depends upon the activity coefficient of the electrolyte. It is for this reason that the theoretical and experimental study of this quantity has received the attention of chemists since the introduction of the fugacity and activity functions by G. N. Lewis<sup>1</sup>. The activity is defined in terms of the chemical potential, thus a study of activity coefficients gives insight into solution thermodynamics.

The theoretical treatment of activity coefficients is based upon a study of the environment of the ions in solution. After many other investigations had fallen short of the desired result, Milner<sup>2</sup> proposed a satisfactory analysis

---

<sup>1</sup>Lewis, G. N., Proc. Am. Acad. Sci., 37, 45(1901);  
43, 259 (1907).

<sup>2</sup>Milner, R., Phil. Mag., 23 551(1912); 25, 742(1913).



of this environmental effect, however, his mathematical treatment was too involved for practical use. Using Debye's conception of the ionic "atmosphere", Debye and Hückel<sup>1</sup> were able to compute activity coefficients for dilute solutions of electrolytes. This theory superceded Milner's in that it employed a mathematical short cut which reduced to a great extent the mathematical complexity of the treatment. It is this theory and extensions of this theory which have been applied to most of the thermodynamic properties in solution.

The limitations of this theory or any other theory of electrolytic solutions must be realized. The application of the results of the Debye-Hückel treatment must be limited to dilute solutions. Electrolytic solutions at concentrations above the limit of validity of the theory must be treated by complicated extensions of the original theory. The concentration limit for accurate application of the theory and the extensions is not high enough to give activity coefficients in the concentration range for which thermodynamic properties are usually needed. It is for this reason that experimental values of activity coefficients are of value. Accurate experimental data not only give information concerning solutions in the desired concentration range, but also afford a means of checking the validity of the theory in dilute solutions and the deviation from ideality in more concentrated

---

<sup>1</sup>Debye, P. and Hückel, E., Physik, Z., 24, 185(1923).

solutions.

Comparison<sup>1</sup> of experimental activity coefficients with those calculated by the Debye-Hückel theory shows that within certain concentration ranges, experiment verifies theory. However, as the concentration increases so does the deviation between theory and experiment. This deviation is more pronounced the greater the charge on the ions. Theoretically, electrolytes of the same type should have activity coefficients which are practically identical for a specified concentration. As a rule this is true in the lower concentration ranges, however, at higher concentrations some electrolytes show highly individual behavior. In these higher concentrations the Debye-Hückel treatment deviates considerably from experimental values because it fails to take into account some individualities of the ions. It is for these electrolytes that it would be of interest to have accurate experimental values for the activity coefficients.

The experimental determination of activity or activity coefficients will depend upon the measurement of some property of the solution which involves these quantities either directly or indirectly. Although there are many methods which apply in principle to the determination of activity coefficients, in practice many of these methods are impractical to apply. The difficulty is obtaining data for

---

<sup>1</sup>Glasstone, S., Thermodynamics for Chemists, D. Van Nostrand Co., Inc., New York, 1947, p. 413.

solutions sufficiently dilute so that accurate extrapolations to infinite dilution are possible. The methods usually used for the determination of activity coefficients of strong electrolytes are: (1) electromotive-force measurements; (2) solubility determinations; and (3) freezing-point determinations. Another method which has been used is the isopiestic method, in which a comparison is made of the concentration of two solutions of equal vapor pressures.

Probably the most direct method for experimental determination of activity coefficients of strong electrolytes is by electromotive-force measurements. The emf of a cell depends upon the free energy change of the cell reaction. Thus, measurement of the emf of a cell affords a direct approach to the activity coefficient. The accuracy of the method will obviously depend upon the ability to obtain reproducible potentials. The latter is dependent upon the ability of obtaining a reversible electrode for the species involved. The absence of experimental activity coefficients for certain electrolytes can be attributed to the inability of securing a suitable electrode for accurate emf measurements.

Probably the outstanding examples of unsuitable electrodes for emf measurements are those of cobalt and nickel. As a result of this, experimental activity coefficients of salts of these metals are extremely scarce in the

literature and those for the sulfates in particular are practically nonexistent. No reference can be found to experimentally determined activity coefficients of cobalt sulfate and Robinson and Jones<sup>1</sup> list values for nickel sulfate only down to 0.1 molal.

This work will be concerned with the determination of the activity coefficients of cobalt sulfate by emf measurements using a saturated cobalt amalgam, a Hg-Hg<sub>2</sub>SO<sub>4</sub> reference half-cell and aqueous cobalt sulfate solution. The measuring setup consists of a Leeds-Northrup Type K-2-potentiometer and a Compton quadrant electrometer as the null-point instrument.

Massive cobalt and other similarly prepared forms of the metal are in a condition of strain which influences the potential to varying extents. The strain persists for an indefinite time and cannot be completely eliminated once it has been set up in the metal. If a saturated amalgam of cobalt in mercury is prepared, this electrode should be free from the objection of strain. Also, if purified mercury is used there should be no objectionable impurities. The use of the Compton quadrant electrometer as the null-point instrument reduces polarization during measurements to a minimum. This is due to the fact that the electrometer operates

---

<sup>1</sup>Robinson, R. A. and Jones, R. S., J. Am. Chem. Soc., 58, 961(1936).

essentially as a galvanometer with infinite resistance and therefore requires no flow of current during measurements.

The Hg-Hg<sub>2</sub>SO<sub>4</sub> reference half-cell was used to eliminate the presence of a junction potential. This is a satisfactory reference provided the solubility of Hg<sub>2</sub>SO<sub>4</sub> is considered in the calculations involving the concentrations of cobalt sulfate.

The object of this study was to arrive at some experimental values for the activity coefficients of cobalt sulfate at various concentrations through emf measurements. The above innovations were used to obtain reproducible potentials. The standard potential for the cobalt amalgam was determined using these potentials and the activity coefficients were calculated using this standard potential.

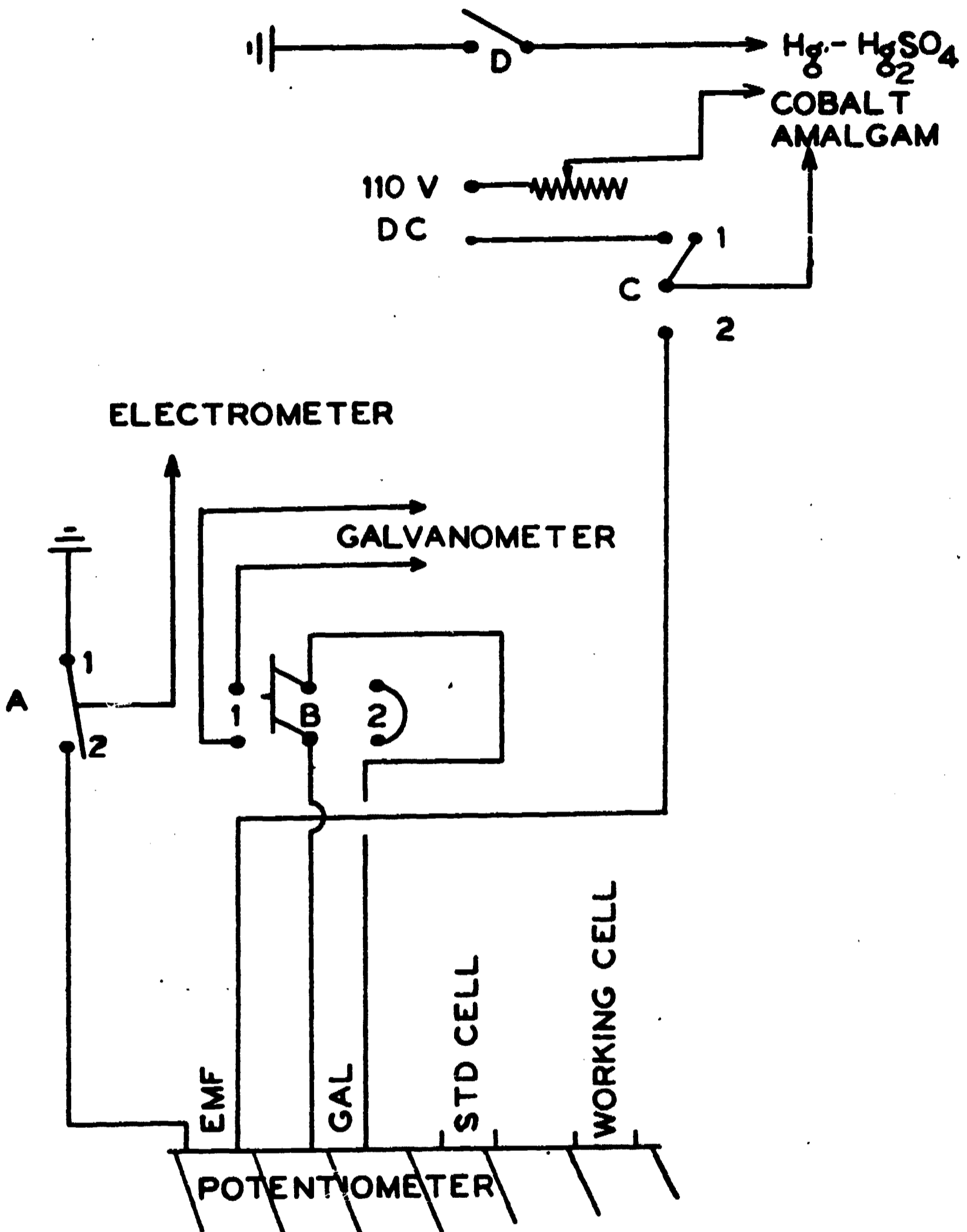
## CHAPTER II

### EXPERIMENTAL

#### Apparatus and Measuring Setup

The potentials listed in the tables of this chapter were measured using a Leeds-Northrup Type K-2 potentiometer and a Compton quadrant electrometer. In conjunction with these instruments, an Eppley Weston standard cell and a 2.0 volt wet cell as the working cell were used. The potentiometer was calibrated with the standard and working cell with a galvanometer. The connections between these instruments are shown in the wiring diagram in Figure 1.

The quadrant electrometer consists of a hollow cylinder with a large radius compared to the height. This cylinder is partitioned into four parts. A vane, charged to a constant potential, is suspended in the hollow of the cylinder from the top. Two of the quadrants are grounded and the emf to be measured is connected to the other two. Measurements are obtained by adjusting the potentiometer so that there is no movement of the vane when switching from the ground connection to that of the unknown emf. This is true when the quadrants are all at the same potential. If



BASIC WIRING DIAGRAM  
FIGURE I

they are at different potentials, a torque is exerted upon the vane and a deflection is observed. The deflections of the vane are observed by reflection of light on a scale from a mirror which is attached to the fiber on which the vane is suspended. In short, the electrometer acts like a galvanometer with a resistance which is essentially infinite.

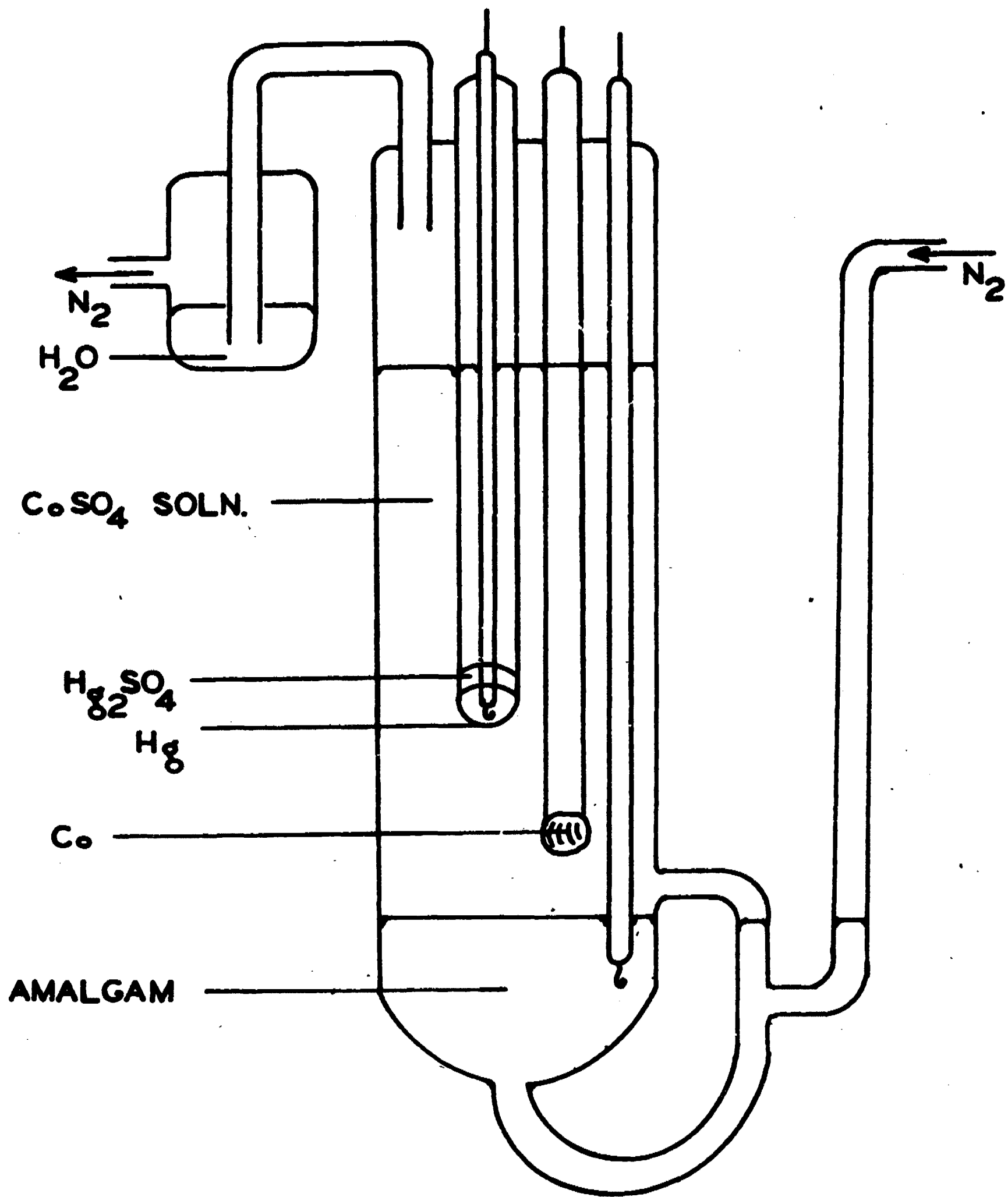
The cells used were of the type shown in Figure 2. They were made with 40 mm test tubes and standard pyrex glass tubing. The cobalt electrode was made by soldering small wire to the cobalt and sealing it with ceresin wax. A rubber stopper was used to seal the cell and to hold the electrodes and water trap for the nitrogen.

The reference electrode was made by blowing a 10 mm opening about one inch from the bottom of a piece of glass tubing sealed at one end. Mercury was placed in the bottom of the tube and covered with  $\text{Hg}_2\text{SO}_4$ . This was placed in the cell and connection made by a Pt electrode sealed in a piece of 2 mm glass tubing which was sealed to the opening of the outer tubing at the top.

Referring to Figure 2, it may be seen that the passage of nitrogen served to stir the amalgam in addition to stirring the solution. Amalgam from the bottom of the cell is "pumped" through the upper opening in the side of the cell during the passage of nitrogen.

Any oxygen which may have been present in the





ELECTROLYTIC CELL  
FIGURE 2

nitrogen was removed by passing the gas over copper turnings which were heated to about 600° C.

All measurements were made at 25° C ( $\pm 0.2^\circ$  C) by immersing the cell in a constant temperature oil bath. The temperature was regulated by a Hg thermostat, "knife" heater and stirrer.

#### Materials and Solutions

The  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  used to make up the cobalt sulfate solution was of reagent grade. Distilled water (pH = 7) was used as the solvent.

The mercury used was of sufficient purity for the measurements concerned. The best check of this was the fact that mercury from two different sources gave results which checked.

$\text{Hg}_2\text{SO}_4$  from three sources was used. These were checked in reference cells and found to agree to  $\pm 0.001\text{V}$  as long as some white  $\text{Hg}_2\text{SO}_4$  remained. Before use it was first washed with concentrated sulfuric acid, then with distilled water, and finally with a solution of the cobalt sulfate used in the particular measurement; the  $\text{Hg}_2\text{SO}_4$  was pure white after this treatment. This procedure proved to give a reproducible Hg- $\text{Hg}_2\text{SO}_4$  half-cell.

Although the metallic cobalt used as the anode in electrolysis was of questionable purity, the results should be affected little if at all. This is because all potential

measurements were made on the amalgam-the purity of which will depend upon the mercury and the electrolytic solution. The amount of nickel in the cobalt metal and in the solution was negligible.

#### Experimental Procedures

A stock solution of  $\text{CoSO}_4$  was made up of about 1 molar concentration. The exact concentration was determined electrolytically by the following procedure: 5 g of  $(\text{NH}_4)_2\text{SO}_4$  and 2 g of hydrazine sulfate were added to 5 ml of the 1 molar cobalt sulfate solution; to this was added 25 ml of  $\text{NH}_4\text{OH}$  and the solution was then diluted to 130 ml. This solution was electrolyzed at about 3 amps until the last tinge of pink disappeared (about 2-3 hours). Platinum gauze electrodes were used. The results obtained were as follows.

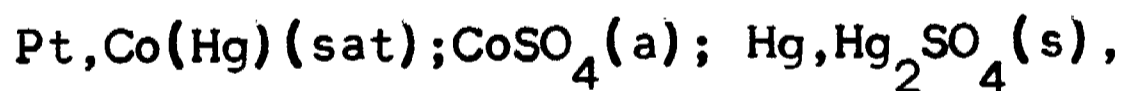
	1	2	3	4
gms of Co/5ml	0.2672	0.2673	0.2673	0.2674
gms of Co/1000ml	53.44	53.46	53.46	53.48
Molarity	0.906	0.907	0.907	0.908

Determinations 1 and 2 were made on the solution when new; determinations 3 and 4 were made toward the end of the research when most of the cobalt sulfate stock solution had been used. The molar concentration used in the calculations is 0.907. All concentrations used were obtained by accurate dilution of this stock solution.

A saturated cobalt amalgam was used for all measure-

ments. The amalgams (denoted in tables by subscripts A, B, C, D, E, and F) were prepared by electrolyzing a 0.1 molar cobalt sulfate solution; cobalt metal was used as the anode and Hg was used as the cathode. Oxygen-free nitrogen was passed through the solution during each electrolysis; this serves to stir the solution, mix the amalgam and keep an inert atmosphere in the cell. Saturation of the amalgam was assumed when the potential (taken as described latter) did not change after further electrolysis. The top portion of all amalgams except D were removed after an initial electrolysis, placed back in the cell and electrolyzed until saturated with cobalt. The electrolyses were carried out with the C switch (Figure 1) in the 1 position and the D switch open to protect the electrometer.

The potentiometer was standardized in the usual manner with the B switch in the 1 position and the potentiometer set to "standard cell". To measure the potential of the cell



switch B was in the 2 position, thus taking the galvanometer circuit of the potentiometer out of the measuring circuit; C was thrown to the 2 position and D was closed; then with the connection on the galvanometer pressed the A switch was thrown from 1(ground) to 2. The potentiometer was adjusted to no deflection of the vane and the emf read from the

potentiometer. The precision of these measurements was  $\pm 0.001\text{V}$ .

### Experimental Results

Several methods of measuring the potential of the cell were tried using 0.0912 molar cobalt sulfate. A summary of the results of these various methods are listed in Table 1 (all potentials in volts). The subscripts A, B, and C refer to different amalgams. The potentials listed were taken under the following conditions: (1) nitrogen and current were turned off simultaneously; (2) nitrogen was passed for the complete 6 hours; (3) nitrogen was passed for the initial 3 hours of measurement; (4) nitrogen was passed for the first 2 hours of measurement; (5) nitrogen was turned off after one hour of measurement. In 7 and 8, nitrogen was passed through the solution for 15 minutes after electrolysis, then turned off, and the potentials measured.

Method 1 is time consuming and the potentials were sometimes quite variable. Passage of nitrogen decreases the time of the drop from the initial potential to the "constant potential plateau" which is the region in which all final values of the potential are eventually taken. However, the "plateau" was found to be quite short when nitrogen is passed continuously after electrolysis for more than an hour as shown in 2, 3, 4, and 5. Even in 6 the constant potential region was somewhat shorter. The procedure which seemed to

give the most consistent results for the shortest time involved was the one used in 7 and 8. This was the procedure used for all data employed in the calculation of the standard potential. The time of electrolysis depended upon the efficiency of the particular electrolysis.

The results obtained by the latter method are listed in Tables II through VI. If this method is used the initial potentials are usually close to the value eventually taken. This is because the constant potential region has been approached closely during the 15 minute passage of nitrogen following electrolysis.

The accuracy and precision of the results are less in the more dilute solutions. This can be attributed to the difficulty of efficient electrolysis and measurement of potentials in dilute solutions. For these reasons, the time involved for obtaining constant potentials increased with decreasing concentrations. The emfs in 10-D and 13-D are probably low because of insufficient electrolysis.

During electrolysis care must be taken so that gases are not given off at the cobalt metal and the amalgam surface. Cobalt metal was used as the anode so that the concentration of the solution would not change during electrolysis. If gases are formed at either of the electrodes during electrolysis, the concentration of the solution will change. For example, if gases appear on the cobalt metal, the deposition

TABLE II

AMALGAM POTENTIALS OF 0.230, 0.183, 0.137  
AND 0.0822 MOLAL  $\text{CoSO}_4$

0.230 Molal								0.183 Molal			
Time (min)	$1_A$	$1_B$	$1_C$	$E_1$	$2_A$	$2_B$	$2_C$	$E_2$			
0	0.978	0.979	0.977		0.978	0.980	0.989				
5	0.977	0.977	0.975		0.977	0.978	0.977				
15	0.975	0.975	0.976		0.977	0.977	0.977				
30	0.976	0.975	0.975		0.976	0.978	0.976				
45	0.977	-----	0.978		0.977	0.977	0.977				
60	0.975	0.975	0.975		0.977	0.976	0.977				
90	-----	0.975	0.975		0.976	0.977	0.977				
120	0.975	0.974	0.974	0.975	0.975	0.974	0.975	0.977			
0.137 Molal								0.0822 Molal			
Time (min)	$3_A$	$3_B$	$3_C$	$E_3$	$4_A$	$4_B$	$4_C$	$E_4$			
0	0.981	0.983	0.982		0.990	0.991	0.989				
5	0.980	0.981	0.980		0.988	0.988	0.989				
15	0.980	0.981	0.981		0.987	0.988	-----				
30	0.980	0.980	0.980		0.986	0.987	0.988				
45	0.980	0.980	-----		-----	0.988	0.988				
60	0.980	0.980	0.980		0.986	0.985	0.987				
90	0.979	0.980	-----		0.987	0.986	0.986				
120	0.979	0.979	0.980	0.980	0.984	0.987	0.983	0.988			

TABLE III

AMALGAM POTENTIALS OF 0.0728, 0.0637, 0.0546  
AND 0.0456 MOLAL  $\text{CoSO}_4$

0.0728 Molal				0.0637 Molal				
Time (min)	5 <sub>A</sub>	5 <sub>B</sub>	5 <sub>D</sub>	E <sub>5</sub>	6 <sub>A</sub>	6 <sub>B</sub>	6 <sub>D</sub>	E <sub>6</sub>
0	0.991	0.993	0.993		0.996	0.999	0.997	
5	0.990	0.991	0.990		0.993	0.995	0.994	
15	0.989	0.991	0.990		0.994	0.994	0.990	
30	0.989	0.986	0.990		0.994	0.994	0.991	
45	0.989	-----	0.989		0.995	0.993	-----	
60	0.990	0.983	0.990		0.994	0.994	0.993	
90	0.988	-----	0.989		0.993	0.992	0.991	
120	0.989	0.985	0.986		0.993	0.990	0.992	
				0.990				0.994
0.0546 Molal				0.0456 Molal				
Time (min)	7 <sub>A</sub>	7 <sub>D</sub>	7 <sub>E</sub>	E <sub>7</sub>	8 <sub>A</sub>	8 <sub>B</sub>	8 <sub>C</sub>	E <sub>8</sub>
0	1.000	0.997	0.995		0.998	1.000	0.998	
5	0.997	0.997	0.994		0.999	1.000	0.999	
15	0.997	0.998	0.990		1.000	0.999	1.000	
30	0.998	0.997	0.988		1.000	1.000	0.999	
45	0.996	0.996	-----		1.001	1.000	1.000	
60	0.997	0.997	0.980		0.999	0.999	0.998	
90	0.996	0.995	-----		-----	0.998	0.996	
120	0.994	0.995	0.961		0.997	0.996	0.995	
				0.997				1.000



TABLE IV

AMALGAM POTENTIALS OF 0.0364, 0.0274, 0.0182  
AND 0.00915 MOLAL  $\text{CoSO}_4$

0.0364 Molal				0.0274 Molal				
Time (min)	$\phi_C$	$\phi_D$	$\phi_E$	$E_9$	$\phi_C$	$\phi_D$	$\phi_E$	$E_{10}$
0	1.000	1.005	1.003		1.006	1.000	1.007	
5	1.002	1.004	1.004		1.008	0.999	1.009	
15	1.004	1.004	1.005		1.009	1.001	1.009	
30	1.004	1.003	-----		1.009	1.003	1.008	
45	1.003	1.002	1.004		1.009	0.998	1.009	
60	-----	1.003	1.000		-----	0.995	-----	
90	1.000	1.001	0.999		1.002	0.997	1.004	
120	0.998	-----	-----		-----	0.995	1.000	
				1.004				1.009
0.0182 Molal				0.00915 Molal				
Time (min)	$\phi_D$	$\phi_E$	$\phi_F$	$E_{11}$	$\phi_D$	$\phi_E$	$\phi_F$	$E_{12}$
0	1.013	1.014	1.013		1.020	1.027	1.029	
5	1.014	1.016	1.015		1.025	1.026	-----	
15	1.016	1.016	1.016		1.026	1.027	1.026	
30	1.015	1.016	1.014		1.026	1.026	1.026	
45	1.014	1.015	1.016		-----	1.026	1.025	
60	1.012	1.013	1.014		1.025	1.023	-----	
90	1.007	1.011	1.013		1.020	1.017	1.020	
120	1.004	1.009	1.011		1.014	-----	1.016	
				1.016				1.026

TABLE V

AMALGAM POTENTIALS OF 0.00825, 0.00735, 0.00645  
AND 0.00556 MOLAL  $\text{CoSO}_4$

0.00825 Molal				0.00735 Molal				
Time (min)	13 <sub>D</sub>	13 <sub>E</sub>	13 <sub>F</sub>	E <sub>13</sub>	14 <sub>A</sub>	14 <sub>C</sub>	14 <sub>D</sub>	E <sub>14</sub>
0	1.021	1.028	1.031		1.029	1.030	1.029	
5	1.025	1.030	1.030		1.030	1.031	1.030	
15	-----	1.030	1.030		1.028	1.030	1.031	
30	1.017	1.028	1.029		1.029	1.029	1.029	
45	-----	1.029	1.031		1.030	1.030	1.030	
60	1.009	1.027	1.030		1.028	1.027	1.029	
90	-----	1.028	-----		1.024	1.028	1.027	
120	1.017	1.025	1.023		1.020	1.024	1.025	
				1.030				1.030
0.00645 Molal				0.00556 Molal				
Time (min)	15 <sub>A</sub>	15 <sub>B</sub>	15 <sub>D</sub>	E <sub>15</sub>	16 <sub>B</sub>	16 <sub>D</sub>	16 <sub>F</sub>	E <sub>16</sub>
0	1.031	1.030	1.035		1.035	1.037	1.034	
5	1.032	1.032	1.033		1.037	1.035	1.036	
15	1.031	1.035	1.032		1.034	1.036	1.035	
30	1.032	1.032	1.031		1.035	1.036	1.036	
45	-----	1.032	1.032		1.036	1.036	1.037	
60	1.032	1.031	1.032		1.033	1.032	1.036	
90	1.029	-----	1.029		1.030	1.034	-----	
120	1.025	-----	1.026		1.024	1.029	-----	
				1.032				1.036

TABLE VI

AMALGAM POTENTIALS OF 0.00469, 0.00293  
AND 0.00123 MOLAL  $\text{CoSO}_4$

0.00469 Molal				0.00293 Molal				
Time (min)	17 <sub>A</sub>	17 <sub>B</sub>	17 <sub>C</sub>	E <sub>17</sub>	18 <sub>C</sub>	18 <sub>E</sub>	18 <sub>F</sub>	E <sub>18</sub>
0	1.038	1.031	1.036		1.041	1.045	1.027	
5	1.039	1.029	1.037		1.037	1.046	1.001	
15	1.039	1.007	1.039		1.032	1.047	0.967	
30	1.037	1.000	1.037		1.021	1.048	0.917	
45	1.036	0.988	1.039		-----	1.047	-----	
60	1.031	0.967	1.037		0.989	1.048	0.821	
90	1.023	0.942	1.031		-----	1.041	-----	
120	1.014	0.920	1.028		0.961	1.030	-----	
				1.039				1.048
0.00123 Molal								
Time (min)	19 <sub>A</sub>	19 <sub>C</sub>	19 <sub>D</sub>	E <sub>19</sub>				
0	1.021	1.027	0.976					
5	1.003	1.029	0.991					
15	1.014	-----	1.013					
30	1.013	1.013	1.010					
45	-----	1.004	0.985					
60	1.009	0.991	0.966					
90	-----	-----	-----					
120	0.997	-----	-----	-----				

of cobalt at the amalgam will exceed the dissolution of the metal at the cobalt anode. This means that the concentration of the solution will be decreased. The reverse of this will occur when gases appear at the amalgam surface. If gases appear at both electrodes during electrolysis, the concentration may or may not change but the uncertainty of concentration and the presence of the gases are undesirable.

It was observed that as the concentration of cobalt sulfate was decreased the current passed during electrolysis must also be decreased in order to prevent the appearance of gases at the electrodes. The range of currents used during electrolysis ranged from 300 - 500 milliamps with the 0.230 molal solution to 10 - 20 milliamps with the 0.00469 molal solution. In order to obtain constant potentials it was necessary to increase the time of electrolysis as the current passed was decreased. This indicates that there was a minimum quantity of cobalt which must be deposited in order to make the cobalt amalgam a reversible electrode.

Many trials were made on the last two concentrations tried - 0.0293 molal and 0.00123 molal. One fairly constant potential was obtained with the 0.00293 molal (18E). However, with an electrolysis current of less than 10 milliamps, gases appeared at the electrodes in the 0.00123 molal solution. The difficulty was due to the fact that the hydrogen overvoltage was probably surpassed before the deposition

potential of cobalt at the amalgam was reached. The voltage necessary to maintain a specified current was found to increase with a decrease in concentration.

During the measurements, the surface of the  $\text{Hg}_2\text{SO}_4$  in the reference cell sometimes turned yellow due to hydrolysis. The effect was more pronounced in the dilute solutions of cobalt sulfate. However, the potential was unchanged as long as some white  $\text{Hg}_2\text{SO}_4$  remained.

The potentials listed in the tables are all in volts. The value of the emf taken for a particular concentration is listed in the last column of each concentration as  $E_i$  where  $i$  is the number given to each concentration.

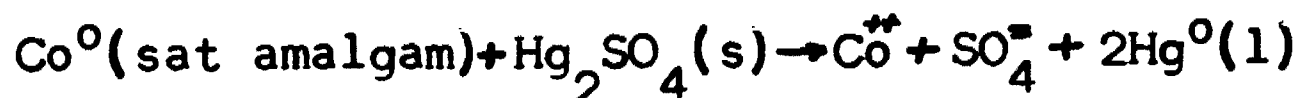
## CHAPTER III

### TREATMENT OF DATA AND RESULTS

The object in mind at the outset of this work was the determination of activity coefficients of cobalt sulfate at various concentrations. This was to be accomplished by the measurement of the emf of a suitable cell containing cobalt sulfate at these concentrations. Once these emfs are determined experimentally, they are used to obtain the standard electrode potential of the cell. This can be seen by considering the cell used:



the cell reaction being,



the emf for which is given by,

$$E = E^0 - \frac{0.05915}{2} \log(a_{\text{Co}^{++}} \cdot a_{\text{SO}_4^{--}}) \quad \underline{A}$$

where  $E^0$  is the standard potential of the given cell and  $a$  represents the activity of the particular ion. These ion activities are related to the molalities  $m$  in the following manner,

$$a_{\text{Co}^{++}} = \gamma_+ m_+ \quad \text{and} \quad a_{\text{SO}_4^{--}} = \gamma_- m_-$$

where

$$m_+ = \text{molality of } \text{Co}^{2+}, \quad m_- = \text{molality of } \text{SO}_4^{2-},$$

and

$$\gamma_+ = \text{activity coefficient of } \text{Co}^{2+},$$

$$\gamma_- = \text{activity coefficient of } \text{SO}_4^{2-}.$$

Thus,

$$a_{\text{Co}^{2+}} \cdot a_{\text{SO}_4^{2-}} = \gamma_+ \gamma_- m_+ m_-$$

By definition the mean ionic molality for  $\text{CoSO}_4$  is given by

$$m_{\pm} = (m_+ m_-)^{1/2}$$

and the mean ionic activity coefficient is given by,

$$\gamma_{\pm} = (\gamma_+ \gamma_-)^{1/2}$$

using the above notation, equation A can be arranged to

$$E + 0.05915 \log m_{\pm} = E^{\circ} - 0.05915 \log \gamma_{\pm} \quad \underline{B}$$

Thus by knowing  $E^{\circ}$  and measuring  $E$  at various molalities,  $\gamma_{\pm}$  can be calculated. If we plot the left side of B versus some function of  $m_{\pm}$ , and extrapolate to  $m_{\pm} = 0$ , then the intercept will be  $E^{\circ}$ , since  $\gamma_{\pm} = 1$  at infinite dilution.

The accuracy of any results depend primarily upon two factors: (1) the accuracy of the experimental data and (2) the method of treatment of the data to obtain the final results. The latter is limited by the precision of the experimental method and the characteristics of the system involved.<sup>1</sup>

There are several methods of extrapolation of vary-

<sup>1</sup>MacInnes, D.A., The Principles of Electrochemistry, Reinhold Publishing Corporation, New York, 1939, p. 156.

ing precision which have been used to obtain  $E^0$ . The method of extrapolation used in this work is of the form used by Hitchcock<sup>1</sup> and Brown and MacInnes<sup>2</sup>. The limitations of this method for concentrated solutions are fully recognized. However, this method proved to give a satisfactory extrapolation of the data in the more dilute concentration range. This will be discussed in more detail in Chapter IV.

The method of extrapolation consists of substituting into equation B the expression

$$-\log \gamma_{\pm} = \frac{AZ_+Z_- \sqrt{\mu}}{1 + Ba_i \sqrt{\mu}} \quad \underline{C}$$

from the Debye-Hückel theory. A and B are constants characteristic of the solvent,  $Z_+$  and  $Z_-$  are the charges on the ions,  $a_i$  is described as the closest distance of approach of the ions, and  $\mu$  is the mean ionic strength which is given by

$$\mu = \frac{1}{2} \sum m_i Z_i^2$$

Substituting C into B we have

$$E + 0.05915 \log m_{\pm} - E^0 = \frac{0.05915 AZ_+Z_- \sqrt{\mu}}{1 + Ba_i \sqrt{\mu}}$$

rearranging and letting

$$E' = E + 0.05915 \log m_{\pm}$$

we have

$$E' - 0.05915 AZ_+Z_- = E^0 - (E' - E^0) Ba_i \sqrt{\mu}$$

For aqueous solutions  $A = 0.5085$  and for cobalt sulfate  $Z_+ = Z_- = 2$ , or

<sup>1</sup>Hitchcock, D.I., J. Am. Chem. Soc., 50, 2076(1928)

<sup>2</sup>Brown, A.S. and MacInnes, D.A., J. Am. Chem. Soc.,



$$E' - 0.1203\sqrt{\mu} = E^0 - (E' - E^0) Ba_1\sqrt{\mu} \quad \underline{D}$$

Defining the following

$$E'' = E' - 0.1203\sqrt{\mu} \text{ and } E''' = (E' - E^0)\sqrt{\mu}$$

D becomes

$$E'' = E^0 - Ba_1 E'''$$

Now a plot of  $E''$  versus  $E'''$  should give  $E^0$  as the intercept and have a slope of  $Ba_1$ . Since  $E'''$  contains  $E^0$ , a preliminary value for this quantity must be obtained. To obtain this we make a preliminary extrapolation of  $E'$  versus  $\sqrt{\mu}$ . This is shown in Figure 3. This gives a value of  $E^0$  of 0.882V which is used in  $E'''$  for a plot of this value with  $E''$ . The  $E^0$  obtained from this extrapolation is used to calculate another series of values of  $E'''$  for another extrapolation. This process is continued until the value of  $E^0$  used to calculate  $E'''$  corresponds with the value of  $E^0$  given by the intercept. The final plot is shown in Figure 4, for which  $E^0 = 0.886V$ . The data for the initial and final extrapolations plus results to be referred to later are given in Table VII. A small correction has been made in the values of  $m_{\pm}$  and  $\mu$  for the solubility of  $Hg_2SO_4$ .

The values for the activity coefficients were calculated using equation B, which may be arranged to give

$$-\log \gamma_{\pm} = \frac{E' - E^0}{0.05915}.$$

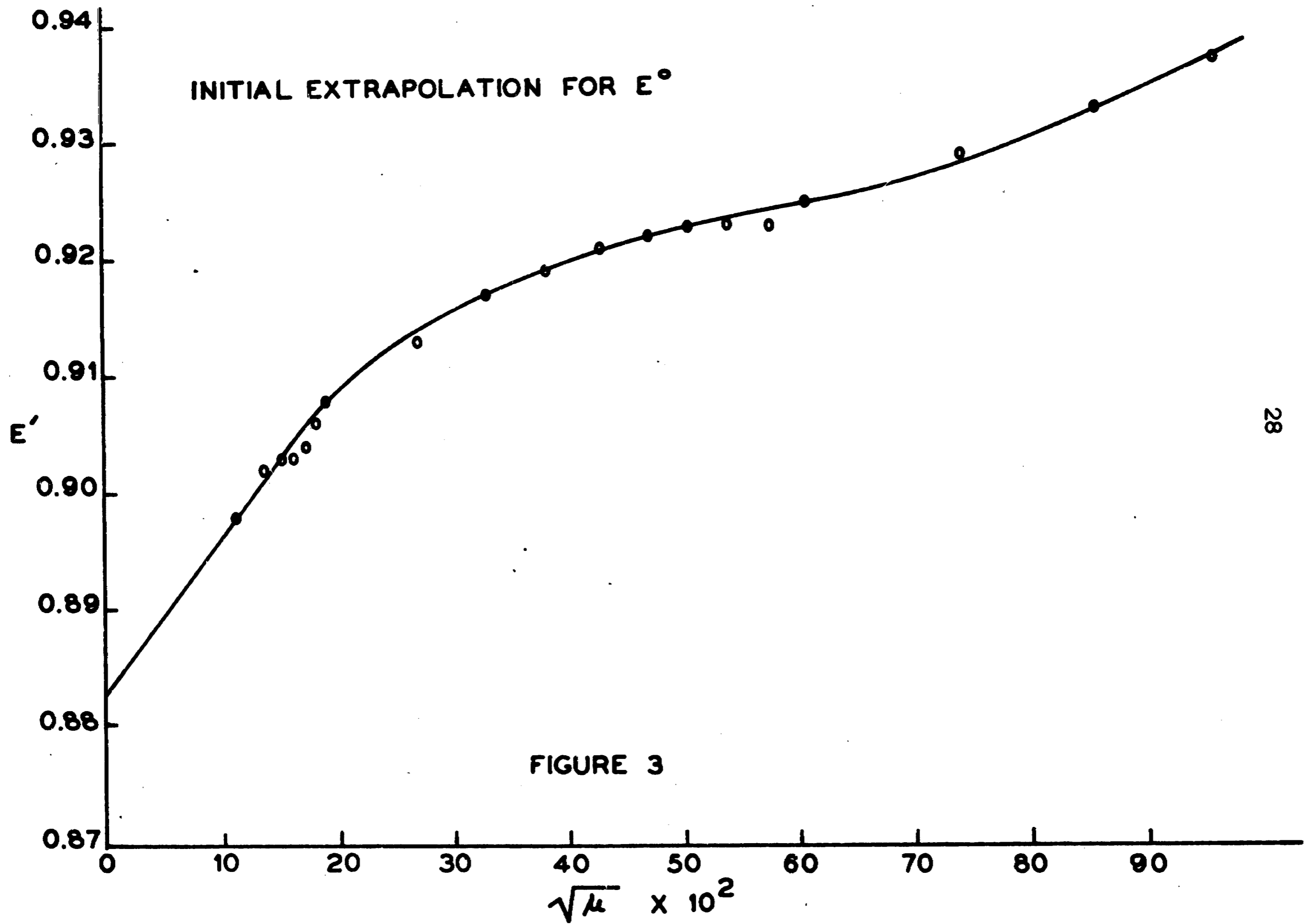
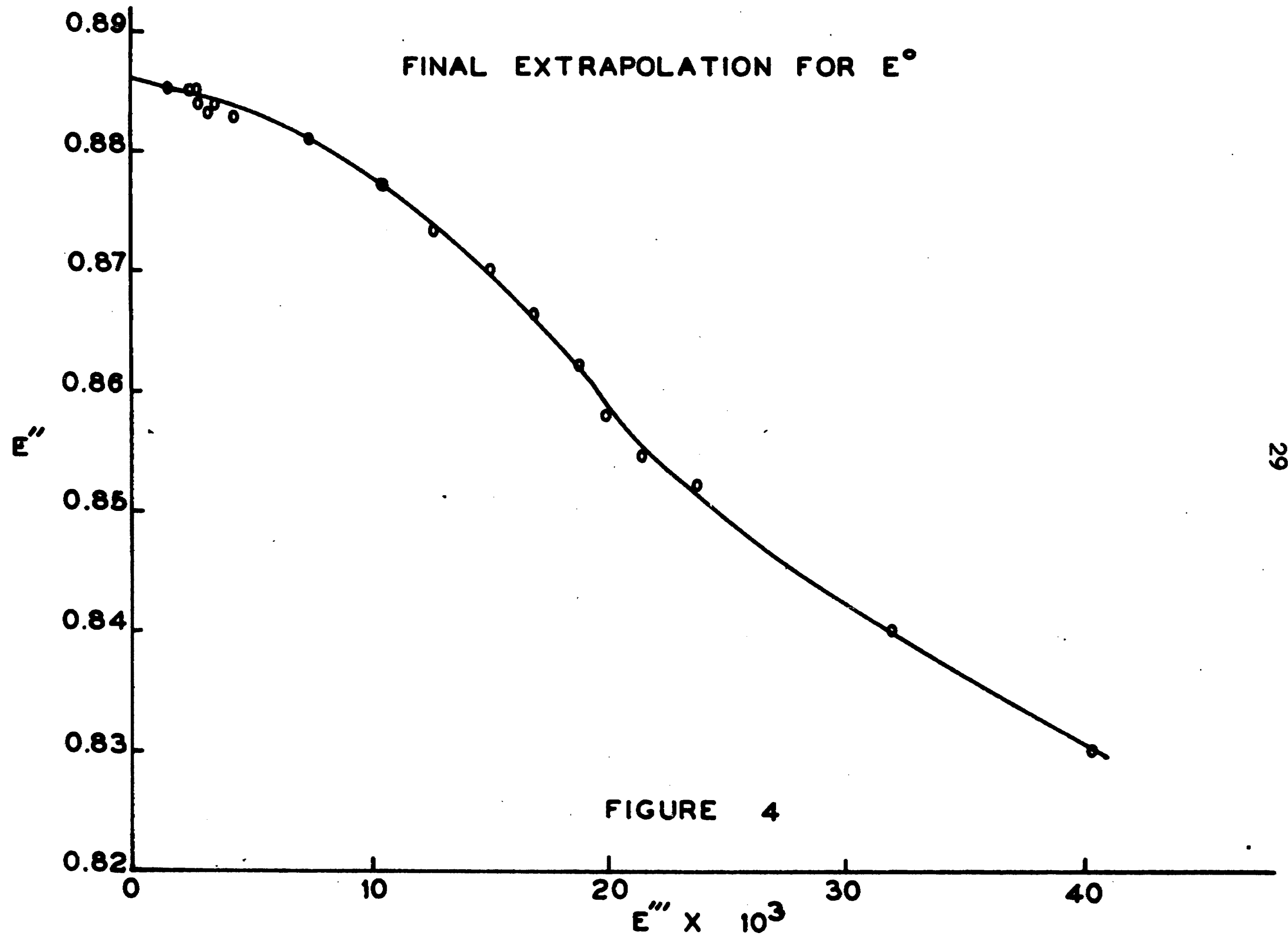


FIGURE 3



**TABLE VII**  
**EXTRAPOLATION DATA AND CALCULATED**  
**ACTIVITY COEFFICIENTS**

$M_{\pm}$	$\sqrt{\mu}$	E	E'	E''	E'''	$\gamma_{\pm}$
0.230	0.959	0.975	0.937	0.821	0.0489	0.137
0.183	0.856	0.977	0.933	0.830	0.0402	0.160
0.137	0.740	0.980	0.929	0.840	0.0318	0.187
0.0912	0.604	0.986	0.925	0.852	0.0236	0.218
0.0822	0.574	0.988	0.923	0.854	0.0212	0.236
0.0728	0.539	0.990	0.923	0.858	0.0199	0.236
0.0637	0.505	0.994	0.923	0.862	0.0187	0.236
0.0546	0.467	0.997	0.922	0.866	0.0168	0.245
0.0456	0.427	1.000	0.921	0.870	0.0149	0.254
0.0364	0.381	1.004	0.919	0.873	0.0126	0.276
0.0274	0.330	1.009	0.917	0.877	0.0102	0.298
0.0182	0.270	1.016	0.913	0.881	0.00730	0.348
0.00915	0.192	1.026	0.906	0.883	0.00422	0.423
0.00825	0.182	1.030	0.906	0.884	0.00364	0.458
0.00735	0.174	1.030	0.904	0.883	0.00314	0.495
0.00645	0.162	1.032	0.903	0.884	0.00275	0.515
0.00556	0.151	1.036	0.903	0.885	0.00256	0.515
0.00469	0.139	1.039	0.902	0.885	0.00222	0.535
0.00293	0.112	1.048	0.898	0.885	0.00134	0.626
0.00123	0.0816	-----	-----	-----	-----	-----

## CHAPTER IV

### DISCUSSION OF METHODS AND RESULTS

#### The Experimental Method

Many investigations<sup>1</sup> have shown the extreme passivity of cobalt in the presence of oxygen, the potential of the metal being lowered in the presence of oxygen. This is particularly true for the amalgam which is extremely sensitive to the presence of oxygen. This explains the necessity for electrolyzing the amalgam to obtain reproducible potentials. This process of cathodic activation has been shown by Kortum and Bockris<sup>2</sup> to reactivate passive metals. They state that there is a current density below which no activation of the passive metal takes place, even though current may flow for a long time. This explains the increasing difficulty in obtaining reproducible potentials after electrolysis in the more dilute solutions and the inability to obtain any stable value in the 0.00123 molal solution.

---

<sup>1</sup>Mellor, J.W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. XIV, Longmans, Green and Co., New York, 1935.

<sup>2</sup>Kortum, G. and Bockris, J., Textbook of Electrochemistry, vol. II, Elsevier Publishing Company, New York, 1951, pp. 461-68.

The potential was initially high following electrolysis due to concentration polarization at the amalgam surface. This was eliminated more rapidly by stirring, as expected. The potential "plateau" was approached much faster if nitrogen was passed following electrolysis.

Tammann and Kollmann<sup>1</sup> observed analogous behavior of the potential of the cobalt amalgam when measured against a calomel half-cell and using a 1 molar  $\text{CoSO}_4$  solution. The potential is initially high and then decreases to become constant for some time and then drop again.

The drop of potential after two to three hours is probably caused by polarization at the amalgam-solution interphase. A type of polarization which could occur is the displacement of  $\text{Hg}_2^{++}$  (from dissolved  $\text{Hg}_2\text{SO}_4$ ) from solution by the cobalt in the surface of the amalgam. This effect would increase with a decrease in concentration of  $\text{CoSO}_4$ , since the concentration of  $\text{Hg}_2\text{SO}_4$  increases as the  $\text{SO}_4^-$  concentration from  $\text{CoSO}_4$  decreases. The reactivity of amalgam electrodes with the electrolyte is noted by Kortum and Bockris<sup>2</sup>. This decrease could also be due partially to the leakage of oxygen into the system.

#### The Amalgam

The properties of the amalgam have not been studied

<sup>1</sup>Tammann, G. and Kollmann, K., Z. fur Anorg. Chemie, 160, 242(1937).

<sup>2</sup>Kortum and Bockris, op. cit., vol. I, pp. 238-52.

extensively. It is a silvery white, spongy material, less fluid than mercury and very unstable when exposed to oxygen for any length of time. The saturated amalgam was observed to be two-phase. The meager studies of the composition of the amalgam in the literature are contradictory. Schumann<sup>1</sup> reports this amalgam prepared electrolytically corresponds to  $\text{Hg}_{10}\text{Co}_{13}$ , although no other investigators have indicated compound formation. Katoh<sup>2</sup> reports on the basis of x-ray data that the amalgam consists of highly dispersed cobalt of  $\alpha$  and  $\beta$  forms in the mercury. Recently Lippert<sup>3</sup> could find only  $\beta$  cobalt present in the amalgam.

The amalgam appears to be a dispersion of cobalt in mercury and therefore the potential of the amalgam should closely approximate that of cobalt. Kortum and Bockris<sup>4</sup> state that the potential of amalgam electrodes will be a little less than that of the pure metal due to interatomic forces operative in amalgams. This latter effect should be a minimum in amalgams of low concentration of the metal. The "solubility" of cobalt in mercury is at the most  $1.7 \times 10^{-1}$  gms of cobalt per 100 gms of mercury<sup>5,6</sup>. Hence, it is im-

<sup>1</sup>Schumann, J., Wied. Ann, 43 106(1891). Mellor, op. cit.

<sup>2</sup>Katoh, N., J. Chem. Soc. Japan, 64, 1211(1943). C.A., 41, 3338(1947).

<sup>3</sup>Lippert, E. L., Personal communication on the basis of x-ray data.

<sup>4</sup>Kortum and Bockris, op. cit., vol. I, pp. 238-52.

<sup>5</sup>Mellor, op. cit.

<sup>6</sup>Booth, H.S., Inorganic Synthesis, vol. I, McGraw-Hill Book Co., Inc., New York, 1939.

probable that the potential of the amalgam is much different from that of cobalt metal.

### The Standard Potential

The standard potential for the cell studied was found to be 0.886V. Taking  $0.615V^1$  as the standard potential of the  $Hg-Hg_2SO_4$  half-cell, we have 0.271V as the standard potential for the cobalt amalgam. Latimer<sup>2</sup> accepts a value of 0.277 as compared to 0.250 for nickel. This was calculated on the basis of the equilibrium between cobalt and nickel and their ions as reported by Heymann and Jellinek<sup>3</sup>. Other values listed in the literature include: 0.253 Neumann<sup>4</sup>; 0.298, Labendzinski<sup>5</sup>; 0.292, Coffetti and Foerster<sup>6</sup>; 0.283, Schildback<sup>7</sup>; 0.246, Lamb and Larson<sup>8</sup>; 0.278, Haring and Westfall<sup>9</sup>.

The value of Lamb and Larson is probably low because no attempt was made to exclude the oxygen of the air. The other values with the exception of that given by Haring and Westfall include junction potentials of unknown value.

<sup>1</sup>Latimer, W.M., Oxidation Potentials, ed. 2, Prentice-Hall, Inc., New York, 1952.

<sup>2</sup>Latimer, W.M., ibid.

<sup>3</sup>Heymann, T. and Jellinek, K., Z. Physik. Chemie, 160, 34(1932).

<sup>4</sup>Neumann, B., ibid., 14, 215(1894).

<sup>5</sup>Labendzinski, S., Z. Elektrochem., 10, 77(1904).

<sup>6</sup>Coffetti, G. and Foerster, F., Ber., 38, 2936(1905).

<sup>7</sup>Schildback, R., Z. Elektrochem., 16, 967(1910).

<sup>8</sup>Lamb, A.B. and Larson, A.T., J. Am. Chem. Soc., 42, 2038(1920).

<sup>9</sup>Haring, M.M. and Westfall, B.B., Trans. Electrochem. Soc., 65, 235(1934).



None of these investigators took into account the polarization which occurs during measurement using the conventional galvanometer as the null-point measuring instrument.

It is possible that the value of 0.271 is a little lower than the standard potential of the cobalt metal. However, the reproducibility of the measured potentials is an indication of their reliability.

The fact that the extrapolation plot of Figure 4 does not conform to the expected curve in the higher concentration region will not effect the value of the extrapolated value for  $E^0$ . The latter is dependent only upon the trueness of the extrapolation near  $m_2 = 0$  and this part of the curve is as predicted. The behavior of the plot in the higher concentration region is an indication of the concentration limitation of the extrapolation used.

#### The Activity Coefficients

The reliability of the calculated values for the activity coefficients do not depend upon closeness of the amalgam potential to the pure metal potential. Looking at the equation from which they are calculated,

$$-\log \gamma_2 = \frac{E' - E^0}{0.005915}$$

we see that they are dependent upon the absolute value of the standard potential of the amalgam and  $E'$ . The latter involves  $E$  and therefore the calculated activity coefficients are dependent upon the measured emfs at the various concen-

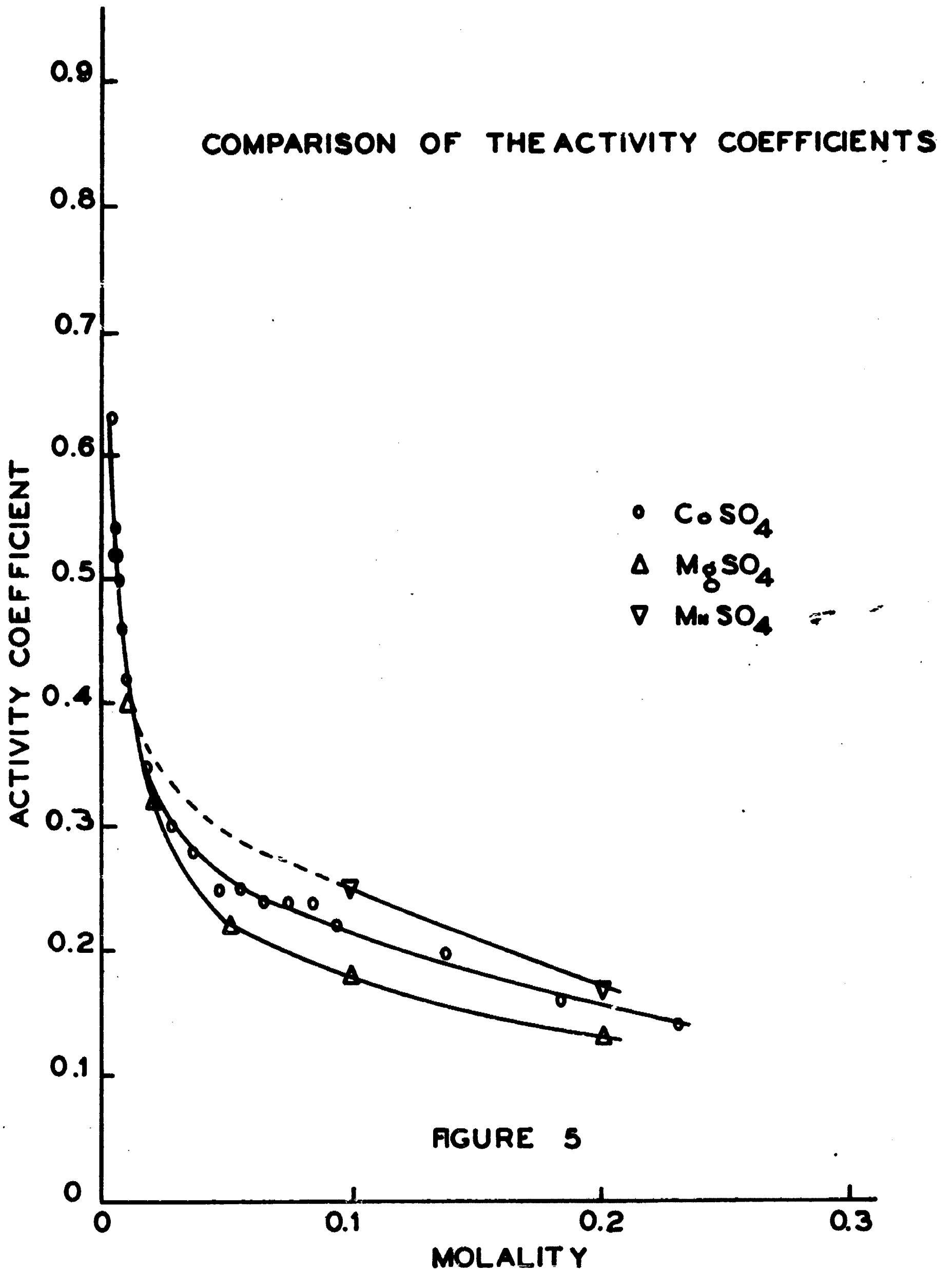
trations. Although there is probably a slight error in the determination of the concentration, it is assumed that this is negligible.

The error involved in the measurement of  $E$  and the determination of  $E^0$  is  $\pm 0.001V$ . This means a probable error of  $\pm 0.02$  in the activity coefficient. The greater the concentration, the less the error of calculation of  $\gamma_{\pm}$ .

The activity coefficients appear to be high, especially above about 0.01 molal. However, this is the region in which there was indication of abnormal behavior of  $CoSO_4$  solutions by the extrapolation plot. Although these activity coefficients are higher for most bivalent sulfates, the similarity of their concentration behavior can be noted in Figure 5 where the determined values for  $CoSO_4$  are compared to those for  $MgSO_4$ <sup>1</sup>. Robinson and Jones<sup>2</sup> determined the activity coefficients of  $MnSO_4$  by the isopiestic method and corroborated these results with freezing point data. The values were 0.25 for a 0.1 molal solution and 0.17 for a 0.2 molal solution of  $MnSO_4$ . For comparison purposes, these two values are also shown in Figure 5.

<sup>1</sup>Latimer, op. cit.

<sup>2</sup>Robinson and Jones, op. cit.



## CHAPTER V

### SUMMARY AND CONCLUSIONS

The standard potential of cobalt amalgam was determined by the measurement of the electromotive force of a cell containing  $\text{CoSO}_4$  solutions. Several innovations were introduced in order to obtain a reproducible potential; (1) an electrometer was used as the null-point instrument to prevent polarization during measurements; (2) a cobalt amalgam was used as the electrode reversible to cobalt; (3) the system was kept under an atmosphere of  $\text{O}_2$ -free nitrogen. The reference cell used was a  $\text{Hg-Hg}_2\text{SO}_4$  half-cell. The emfs taken were those on a "constant potential plateau" which followed an electrolysis by about thirty minutes to an hour. The range of concentrations was from 0.230 molal to 0.00123 molal. The measurements became increasingly difficult as the solutions became more dilute. This was due to the inability to electrolyze with a high enough current density, the probability of increasing polarization, and the usual difficulty of potential measurements in dilute solutions. All measurements were made at  $25^\circ\text{C}$ . Using the emfs measured at various concentrations and extrapolating according to the

Hitchcock and Brown and MacInnes method an  $E^0$  of 0.271V was obtained for the cobalt amalgam. This value compares fairly satisfactorily with  $E^0$  of cobalt as listed by other investigators but is a little low. Any detailed comparison awaits further study of the relationship between potentials of cobalt and similar metals and their amalgams.

The reproducibility of the emfs indicates the reliability of the choice of the cobalt amalgam as the electrode reversible to cobalt. However, the cobalt amalgam and similar amalgams need special experimental treatment to insure that they behave as reversible and reproducible electrodes.

The method of extrapolation, although open to some question at high concentrations, gave satisfactory results at the lower concentrations. The non-conformity of the extrapolation plot in the higher concentration region is no more than expected. In the first place, the expression of the Debye-Hückel theory is not strictly applicable in this region, especially for 2-2 electrolytes. Secondly,  $\text{CoSO}_4$  solutions probably exhibit some individuality at these higher concentrations which is not taken into account in this treatment. However, the activity coefficients only depend upon the accuracy of the extrapolation in the lower concentration region and may actually be taken as a measure of some characteristic peculiar to the salt at high concentra-

Hitchcock and Brown and MacInnes method an  $E^{\circ}$  of 0.271V was obtained for the cobalt amalgam. This value compares fairly satisfactorily with  $E^{\circ}$  of cobalt as listed by other investigators but is a little low. Any detailed comparison awaits further study of the relationship between potentials of cobalt and similar metals and their amalgams.

The reproducibility of the emfs indicates the reliability of the choice of the cobalt amalgam as the electrode reversible to cobalt. However, the cobalt amalgam and similar amalgams need special experimental treatment to insure that they behave as reversible and reproducible electrodes.

The method of extrapolation, although open to some question at high concentrations, gave satisfactory results at the lower concentrations. The non-conformity of the extrapolation plot in the higher concentration region is no more than expected. In the first place, the expression of the Debye-Hückel theory is not strictly applicable in this region, especially for 2-2 electrolytes. Secondly,  $\text{CoSO}_4$  solutions probably exhibit some individuality at these higher concentrations which is not taken into account in this treatment. However, the activity coefficients only depend upon the accuracy of the extrapolation in the lower concentration region and may actually be taken as a measure of some characteristic peculiar to the salt at high concentra-

tions which the Debye-Hückel expression does not allow for in the limiting form used.

The measured emfs and the value obtained for the standard potential were used to calculate activity coefficients for  $\text{CoSO}_4$  at the various concentrations. These activity coefficients are not dependent upon the standard potential of cobalt being the same as the standard potential of the cobalt amalgam. The calculated activity coefficients of  $\text{CoSO}_4$  appear to be high in the high concentration range but are comparable in behavior to other bivalent sulfates and are lower than the activity coefficients of manganese sulfate at 0.2 and 0.1 molal concentration.

## BIBLIOGRAPHY

- Booth, H. S., Inorganic Synthesis, Vol. I, McGraw-Hill Book Company, Inc., New York, 1939.
- Brown, A. S. and MacInnes, D. A., J. Am. Chem. Soc., 57, 1356(1935).
- Coffetti, G. and Foerster, F., Ber., 38, 2936(1905).
- Debye, P. and Huckel, E., Physik. Z., 24, 185(1923).
- Glasstone, S., Thermodynamics for Chemists, D. Van Nostrand Company, Inc., New York, 1947.
- Haring, M. M. and Westfall, B. B., Trans. Electrochem. Soc., 65, 235(1934).
- Heymann, T. and Jellinek, K., Z. Physik, Chemie, 160, 34(1932).
- Hitchcock, D. I., J. Am. Chem. Soc., 50, 2076(1928).
- Katoh, N., J. Chem. Soc. Japan, 64, 1211(1943).
- Kortum, G. and Bockris, J., Textbook of Electrochemistry, Vol. I and II, Elsevier Publishing Company, New York, 1951.
- Labendzenski, S., Z. Elektrochem., 10, 77(1904).
- Lamb, A. B. and Larson, A. T., J. Am. Chem. Soc., 42, 2038(1920).
- Latimer, W. M., Oxidation Potentials, ed. 2, Prentice-Hall, Inc., New York, 1952.
- Lewis, G. N., Proc. Am. Acad. Sci., 37, 45(1901), 43, 259(1907).
- Lippert, E. L., Personal Communication.



- MacInnes, D. A., The Principles of Electrochemistry, Reinhold Publishing Corporation, New York, 1939.
- Mellor, J. W., A. Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XIV, Longmans, Green and Company, New York, 1935.
- Milner, R., Phil. Mag., 23 551(1912); 25, 742(1913).
- Neumann, R., Z. Physik Chemie, 160 34(1932).
- Robinson, R. A. and Jones, R. S., J. Am. Chem. Soc., 58, 961(1936).
- Schildback, R., Z. Elektrochem, 16, 967(1910).
- Schumann, J., Wied. Ann, 43 106(1891).
- Tammann, G., and Kollmann, K., Z. fur Anorg Chemie, 160, 242(1937).