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Approved by:

Wayland M. Burgess.
Robt. C. Cautelo.

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THE FACTORS AFFECTING THE ELECTRODE POTENTIAL OF COBALT

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degree of

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by

Leslie German

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M.S. Lafayette College 1927

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INTRODUCTION AND THEORY

The classical investigations of Nernst(1) led to the development of his well known osmotic theory of electrode potentials and to his concentration cell formula; and also made possible the definition of the normal electrode potential. Electromotive forces at the electrodes are commonly called electrode potentials. The electrode potential of a half cell in which all substances involved are at unit activity* is known as the normal electrode potential of the half cell.

The conception, that electromotive forces are due to electrolytic solution pressure, can be attributed to Nernst. He assumed that when a metal is placed in water or in a solution, there is a tendency for the metal to pass from the atomic state to the ionic state; and that the equilibrium resulting between a metal and a solution of its ions is between the constituent and the metal ions.

Let us assume that a metal possesses a definite ion solubility, S, and that this metal is placed in an aqueous solution containing ions at a concentration, C, where C equals the concentration of the metal ions in the solution. There are three possibilities:

1. $S > C$

If S is greater than C, metal ions dissolve, the metal

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* The activity of a chemical substance is that quantity which when substituted in the Law of Mass Action expression and in other thermo-dynamic equations expresses the actual mass action effect.

is left negatively charged and the solution possesses excess positive charges. Therefore it is charged positively. The now negatively charged metal attracts positive charges and a potential*, ψ, is set up at the interface. Both the negative charge on the metal and the positive charge in solution tend to prevent positive ions from going into solution. The metal ions continue to dissolve and the electric field, due to the positive and negative charges, increases in strength until equilibrium is reached, i.e., a potential exists at the surface of the electrode and the electric field balances the tendency of ions to dissolve.

2. $S < C$

If S is less than C there is an electric field set up at the interface and again a potential exists.

3. $S = C$

If S equals C there is equilibrium and hence no electric field.

The equation due to Nernst, developed from the above ideas, which expresses the single electrode potential E, in terms of the electrolytic solution pressure P and osmotic pressure p, is as follows:

$$E = \frac{RT}{nF} \ln \frac{p}{P}$$

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* Potential is defined as the work done against inter-ionic forces by a unit charge in passing the interface from a point within the metal to a point in solution. Potential will be designated by ψ.

where; F = Faraday = 96,500 coulombs
R = gas constant = 8.316 joules per degree
T = absolute temperature
n = valence of ion

The difference of the single electrode potentials gives the electromotive force of a voltaic cell, that is,

$$E = E_1 - E_2$$

where E = electromotive force of the cell and E_1 and E_2 are electrode potentials of half cells.

Thus when measured by the potentiometer method the electromotive force of a cell is equal to the algebraic difference of the contact differences of potential. In the determination of single electrode potentials, E_2 is the electrode potential of the reference cell and it is arbitrarily given the value of zero if the reference cell is the half cell, H_2 (g, 1 atmos.), H^+ ($a^{\pm *}$ = 1) molal. In actual practise, however, a half cell of known reproducible value is used, usually a calomel or mercurous sulphate half cell, this cell being referred in turn to the hydrogen half cell.

Compilations of tables of standard normal potentials were made in 1900 by Wilsmore,(2) and in 1911 by Abegg, Auerbach and Luther.(3)

By using more exact theoretical methods and attaining greater experimental precision, G. N. Lewis(4) and his

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* a = activity

colleagues have increased the accuracy of the values of standard potentials to a very great extent. The introduction of the activity function by Lewis, has placed the thermo-dynamics of solutions on a more exact basis and has made possible a more exact treatment of the galvanic cell and electrode potentials.

Consider the general electrode reaction:

a mols A (at a_A)$+$b mols B (at a_B)$+ \ldots\ldots + n \oplus \longrightarrow$
e mols E (at a_E)$+$f mols F (at a_F)

where a = activity

$$-\Delta F = EnF$$

where,

$-\Delta F$ = decrease in free energy

E = electrode potential of half cell as written

n = valence

F = Faraday = 96,500 coulombs

Consider the following process:

1. Transfer a mols A from activity a_A to a = 1, an infinite quantity of solution being understood, then,

$$-\Delta F_1 = aRT\ln\frac{a_A}{1} = RT\ln a_A^a$$

2. Transfer b mols B from a_B to a = 1

$$-\Delta F_2 = bRT\ln\frac{a_B}{1} = RT\ln a_B^b$$

3. Bring about a change in state from a_A at $a_A = 1$ and b_B at $a_B = 1$ to eE at $a_E = 1$ and fF at $a_F = 1$ by means of normal electrode reactions.

$$aA(a_A = 1) + bB(a_B = 1) + \ldots . n e \longrightarrow eE(a_E = 1) + fF(a_F = 1)$$

$$-\Delta F_3 = E^o n\ F$$

where

$$E^o = \text{normal electrode potential.}$$

4. Transfer e mols E at $a_E = 1$ to $a_E = a_E$

$$-\Delta F_4 = eRT\ln \frac{1}{a_E} = -RT\ln a_E^e$$

5. Transfer f mols F from $a_F = 1$ to $a_F = a_F$

$$-\Delta F_5 = fRT\ln \frac{1}{a_F} = -RT\ln a_F^f$$

The net result:

$$-\Delta F = \sum(-\Delta F) = \underbrace{E^o n\ F}_{3} + \underbrace{RT\ln a_A^a\ a_B^b}_{1,2} - \underbrace{RT\ln a_E^e\ a_F^f}_{4,5}$$

$$= E^o n\ F - RT\ln \frac{a_E^e\ a_F^f}{a_A^a\ a_B^b}$$

$-\Delta F = EnF$ where $E =$ electrode potential when activities are a_A, a_B ......

$$\therefore \quad EnF = E^o n\ F - RT\ln \frac{a_E^e\ a_F^f}{a_A^a\ a_B^b}$$

$$E = E^{o} - \frac{RT}{nF} \ln \frac{a_E^{e}\, a_F^{f}}{a_A^{a}\, a_B^{b}}$$

The electrode of the half cell whose potential is to be measured must be both reversible and reproducible.

A reversible process may be defined as a process of which every state is in a condition of stable equilibrium. Similarly, a reversible cell may be defined as a cell every state of which is in a condition of equilibrium. In reversible cells all substances must be in their most stable state.

"Polarization is an influencing factor in the experimental determination of the reversible electromotive force. It involves certain time factors such as velocities. Electrodes are generally considered satisfactory if a current of the order 10^{-8} or 10^{-9} amperes produces no sensible polarization. The measured electromotive is then independent of the direction of the small current used in the measurements, and may be taken as equal to the reversible electromotive force.

To this class belong most electrodes of the common metals in solutions of their salts, except solutions in which we meet the still mysterious phenomenon of passivity, which may ultimately prove to be a phenomenon of polarization. The phenomena which occur at boundary surfaces influence contact potentials. These phenomena, which include overvoltage and passivity, are for the most part obscure."(4)

The potentials of metals depend to a very large extent on the physical structure and state of the metal. It is well known that the physical state of metals deposited electrolytically is influenced by various factors such as the acidity of the plating solutions and the current density employed during deposition; and that their potentials with respect to their ions vary accordingly.

Two plates of the same metal, immersed in a solution of the same salt of that metal, give a difference of potential which amounts in extreme cases to tenths of a volt. If the metal is pure such a difference can hardly be ascribed to any other cause than a variation in the physical state of the metal, or at least of its surface. Any treatment such as produces surface strain has a marked effect on the electrode potential.

It has been found experimentally(5) that the softer metals have less surface strain and the alkali metals form electrodes of a higher constancy and reproducibility than have been attained with any other solid metals.

Finely divided metal seems to give satisfactory results, to possess a constancy and reproducibility, and presumably gives the potential which is characteristic of the metal in its most stable state.(6)

HISTORICAL

In the compilation of normal electrode potentials made by Wilsmore(7) in 1900, cobalt is given the value of +0.232 volts* with reference to the normal electrode potential of hydrogen taken as zero. This value was calculated from the work of Neuman,(8) who used the cell $Co/CoSO_4/KCl/Hg$, and employed as the electrode, electrolytic cobalt deposited from a cobalt ammonium chloride boric acid solution. He emphasized the importance of using nickel free salts.

In 1904, Labendzinski(9) obtained E^o for cobalt, +0.262 volts. Cofetti and Foerster,(10) in 1905, published the results of their experiments and fixed the value for E^o equal to +0.292 volts for cobalt.

Kistiakowsky,(11) using Wilsmore's table, calculated some potentials, one of which was based on the experimental results of LeBlanc.(12) LeBlanc found the potential of cobalt to be +0.45 volts using cobalt against a normal cobalt sulphate solution.

Schildbach(13) found the value +0.293 volts for the difference of potential between cobalt and a normal solution of the chloride, measured in an atmosphere of nitrogen, and +0.339 volts for 0.1 N. cobalt chloride solution. For the sulphates the corresponding values were +0.316 volts and +0.339 volts as compared with the normal hydrogen electrode. These values were obtained with cobalt powder; the massive

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* The American Convention will be used throughout this paper.

metal gave less positive values, 0.288 volts in normal cobalt sulphate, for example. Cobalt powder charged with hydrogen gave considerably more positive values at first which gradually changed until the equilibrium potential was reached. The value given in the International Critical Tables,(14) calculated with reference to the normal hydrogen electrode is $E^{o} = +0.307$ volts.

Stuhlman(15) also ascribes the variations in contact difference of potential of a specific metal primarily to the kind and concentration of the occluded gas. He found that ozone, oxygen, air, carbon dioxide, nitrogen, hydrogen, and ammonia, if occluded by a metal, shifts the position of the metal in the Volta series to a more electro-positive value, in the order in which they are named. Successive increases in the concentration of the gas occluded in the metal produces successive decreases in the electro-negative magnitude of the contact potential difference.

From another table published by Abegg, Auerbach, and Luther(16) the value +0.29 volts is listed as the normal potential of cobalt.

The potentials of six cobalt ammines were measured in 3.27 N. ammonium hydroxide by Lamb and Larson.(17) They prepared a number of cobalt electrodes by electroplating on platinum and carbon from solutions of cobalt chloride in water, in boric acid solution, and in ammoniacal solution.

Using the cell $Co_{(s)}/CoCl_2$ soln./NKCl/$HgCl_{(s)}$/Hg(l), they obtained $E^o = +0.255$ volts. Although they obtained potentials which remained constant within a millivolt over many hours, or even many days, they specifically state that the electrodes usually exhibited individual variation.

Recently Heymann and Jellinck(18) investigated the equilibrium $Ni + Co^{++} \rightleftharpoons Ni^{++} + Co$. The equilibrium was investigated in aqueous nitrate solutions at 25° C. At equilibrium $\frac{Co^{++}}{Ni^{++}} = 8 \pm 5\%$ which, combined with the normal electrode potential of Ni^{++} gave $+0.268$ volts for E^o Co^{++} at 25° C.

For convenience the following table lists the values found for the normal potential of cobalt together with the investigators.

TABLE I

Investigator	Normal Potential E^o in volts	Remarks
1. Neuman	$+0.232$	Salt bridge, double cobalt salt used for plating, electrolyte $CoSO_4$.
2. LeBlanc	$+0.450$	Electrolyte N. $CoSO_4$
3. Labendzinski	$+0.262$	Cobalt electrode deposited from Cobalt Chloride soln., HgO/Hg reference cell electrolyte $CoSO_4$
4. Cofetti & Foerster	$+0.292$	Measurements at 20° N. $CoSO_4$ electrolyte.
5. Schildbach	$+0.307$	Measured in atmosphere of nitrogen.
6. Abegg, Auerbach, Luther	$+0.290$	
7. Lamb & Larson	$+0.255$	Cell Co/$CoCl_2$ soln./N.KCl/HgCl/Hg
8. Heymann & Jellinck	$+0.268$	$\frac{Co^{++}}{Ni^{++}}$ equilibrium in aqueous nitrate solution.

Various reference electrodes have been used. This, however, is a minor factor, for as long as the reference electrodes are reversible and reproducible they may readily be referred to the arbitrary standard, the hydrogen electrode.

Liquid junctions exist in all of the cells; and since the junction potentials have not been taken into account, the accuracy of the values is not of the highest order.

Hydrogen has not been avoided always, thus tending to give too negative results.

The methods of preparing the electrodes also vary. In the majority of cases electrolytic metal has been used; but even then the composition of plating baths, current densities, temperature, etc., were not uniform. As the state and structure of the metal is perhaps the most inportant factor in determining the potential of the metal, the method of preparation of the electrodes in all probability accounts for the variance of the values given in the above table for the normal potential of cobalt.

Considering the other members of the "Iron Group", we find that the best value for nickel seems to be that given by Haring and Bosche,(19) namely +0.231 volts, but values varying from +0.138 to +0.621 are given in the literature. Newberry(30) working with nickel found that impurities in the metal had no marked influence on the potential of the metal also that oxygen is an unimportant impurity, contrary to opinion of most investigators. He explained the wide variation in values by a theory of allotropy and hydration of nickel ions.

The value for the potential of iron given in the International Critical Tables is +0.4410 volts. Recently, Randall and Frandsen(21) have re-determined the single potential of iron and they give as a better value +0.4402 volts.

Thus with respect to the "Iron Group" cobalt occupies a position between iron and nickel.

OBJECT

The object of this investigation was to make a detailed study of the factors affecting the electrode potential of cobalt.

EXPERIMENTAL

A. Materials

1. Water

Conductivity water was used in the preparation of all solutions. This was the best product of a Precision electric still and was found to have a specific conductivity of 1.74×10^{-6} reciprocal ohms.

2. Cobalt Sulphate

Kahlbaum's nickel-free cobalt sulphate was used for all solutions, both for the electrolyte of the cells and for the plating solutions.

3. Cobalt

(a) Reduced metallic cobalt

The metallic cobalt was obtained by reduction of the oxide according to Kalmus,(22) the experimental details of the preparation of the oxide being based on the method of Chaudron.(23)

The cobalt oxide was placed in an alundum boat, which in turn was placed in a pyrex tube. This tube was fitted with one-hole stoppers at each end through which two 5 cm. lengths of 4 mm. glass tubing were passed to provide an inlet and outlet for the hydrogen.

The hydrogen used was purified by passing the gas from a cylinder, through sulphuric acid, an alkaline solution of potassium permanganate, then over hot reduced copper, thence into the tube containing the charge of oxide. The excess hydrogen was burned after leaving the pyrex tube.

The oxide was heated at 500°C. for seven hours and gave a product analyzing 99% cobalt. This cobalt was used to cover the plated electrode.

(b) Plated Cobalt

The cobalt for the electrode proper was prepared by electrolytic deposition from various plating baths, using various plating surfaces and current densities.

(1) Kalmus, Harper and Savell(24) investigated various plating baths and suggested the following for the most successful results for thin deposits.

(a) 200 gms. cobalt ammonium sulphate, $CoSO_4(NH_4)_2SO_4.6H_2O$, equivalent to 145 gms. of anhydrous salt in one liter of water.

(b) 319 gms. cobalt sulphate
19.6 gms. sodium chloride
Boric acid nearly to saturation in one liter of water.

(2) Winkler,(25) who prepared a specimen of pure cobalt for atomic weight determinations found the following solution successful.

100 cc. cobalt sulphate solution containing 11.62 gms. of cobalt per liter.

30 gms. NH_4OH (specific gravity 0.905)

500 cc. water.

The metal obtained in this way contains a small quantity of the oxide but this may be reduced by heating in a current of hydrogen.

(3) Neutral solutions of cobalt sulphate 2.5 N.

(4) Ammoniacal solutions of cobalt sulphate 2.5 N.

4. Mercury

The mercury used was purified by Kowalewski.(26) Mercury in dilute nitric acid was stirred continuously for a week or longer. This method was shown to be superior to the usual method of merely dropping mercury through a column of dilute nitric acid - mercurous nitrate mixture and to distillation.

5. Mercurous Sulphate

The mercurous sulphate was prepared according to the method of Hulett.(27) Pure mercury and sulphuric acid (density 1.15) were electrolyzed between a mercury anode and a platinum cathode. Mercurous sulphate is formed and goes into solution at the anode but when the acid is saturated (2 gms. Hg_2SO_4 /Liter) solid mercurous sulphate appears and covers the anode. At the cathode, hydrogen is liberated and a small amount of mercury. The efficiency is very great, however, about nine grams of the salt being formed per ampere hour. If the mercurous sulphate is allowed to collect on the anode to any great extent, a secondary reaction may take place. This is to be avoided and an electrical stirrer was used to keep the mercurous sulphate in suspension while the current was passing.(28)

B. Preparation of Solutions

All solutions were prepared from nickel-free cobalt sulphate (Kahlbaum) and conductivity water. The preparation of these two materials have been described above.

A fresh solution was prepared for each determination. The concentration of the solutions were determined by analysis of solutions from the half cells.

C. Analytical Method

Volumes of solutions containing 0.15 gms. to 0.25 gms. of cobalt, that could be analyzed conveniently by the electrolytic method, were electrolyzed according to the method of Lindell and Hoffman,(29) modified by Payne.(30)

For the more dilute solutions, the analyses were made by density determinations. The details of determining the densities of the solutions together with a formula for calculating normalities are given by Payne.(31)

D. Experimental Method

1. Apparatus

(a) For the measurements of the potentials exclusive of the series measurements a Leeds and Northrup student potentiometer was used with a portable galvanometer.

For the series measurements, a Leeds and Northrup(32) Type K potentiometer, telescope and scale galvanometer (sensitivity 200 meg.) and standard cell were used.

(b) Half cells of the conventional design were employed.

(c) Several electrodes were tried.

1. Platinum rod plated with cobalt.
2. Platinum rod plated with cobalt and surrounded with finely divided cobalt metal.
3. Platinum rod plated with cobalt and completely covered with finely divided cobalt metal.
4. Platinum gauze (very fine) plated with cobalt.

The last electrodes mentioned gave the most satisfactory results. These electrodes were flat pieces of fine platinum gauze about 1.5 cms. in diameter, they were welded to pieces of platinum wire, then sealed into the ends of 18 cms. lengths of 4 mms. glass tubing. Contact was made by filling these glass tubes with mercury.

(d) The cells were kept in a water thermostat which was maintained at a temperature of 25°C.. 0.02° by means of a toluene-bulb-mercury gas thermo-regulator, which operated a micro gas burner, the bath being stirred by a low speed motor. Cooling water was run through a copper coil.

(e) All volumetric apparatus was calibrated at 25°C.

E. Factors Affecting Electrode Potentials

1. Nature of Electrode

Cobalt was plated on a rod of platinum approximately 1.5 cms. long and 0.1 cms. in diameter from the various solutions mentioned under materials.

In order to determine the most satisfactory bath, current, and time of plating, experiments were performed. The results of these experiments appear in Table II.

TABLE II

Electrode	Current Used (amperes)	Plating Solution	Time (hrs)	Nature of Deposit
1	0.1	Winkler's soln.	3	Rough gray deposit, blackened after 3 hours crystalline growths appeared at end of rod
2	0.1	"	4	very crystalline deposit
3	0.2	$CoSO_4$(approx. 0.5 gms) 100 cc soln.(40 cc H_2SO_4 220 NH_4OH) Soln 1	4	Fine smooth deposit. After 3 hours crystalline growths started to deposit on end of rod
4	0.1	Soln. 1	3	Smooth deposit
5	0.04	"	3	No satisfactory deposit
6	0.05	"	3	Smooth gray deposit
7	0.10	Soln + $NaHSO_3$	3	Smooth deposit

From the results shown in Table II satisfactory plates of cobalt may be obtained on platinum rod using 50 to 100 milliamperes for a period of 3 hours, and an ammoniacal solution of cobalt sulphate.

The plated electrodes were surrounded by a small amount of metallic cobalt and readings were taken of the cell $Co_{(s)}, CoSO_{4(c)}, Hg_2SO_{4(s)} \neq Hg(l)$.

Readings were also taken with half cells containing plated electrodes which were entirely covered with the metallic cobalt.

Solutions used in all the cells were 0.5 normal.

TABLE III

Cell No.	Condition Electrode	Plating Soln.	Conc. $CoSO_4$	Days 1	2	3	4	5	6	7
1	plated electrode	Neutral Soln.	0.5N	0.895	0.902	0.903	0.905			
2				0.927	0.935	0.940				
3	"	"	"	0.904	0.908	0.915	0.922	0.928	0.933	0.933
4				0.910	0.909	0.917	0.925	0.940	0.930	0.931
5	"	ammoniacal		0.951	0.948	0.948	0.948	0.948		
6			"	0.944	0.962	0.959	0.960	0.958		
7	"			0.934	0.935	0.933	0.933	0.932	0.933	
8	surrounded by small amt.cobalt	"	"	0.955	0.935	0.935				
9	"	"	"	0.931	0.929	0.930	0.929	0.934	0.937	0.930
10				0.945	0.933	0.920	0.930	0.934	0.932	0.934
11	plated electrode entirely surrounded with cobalt	"	"	0.987	0.987	0.982	0.981	0.980	0.980	0.980
12				0.949	0.945	0.871	0.860	0.860	0.860	0.859

The results tabulated in Table III indicated that the plated electrodes (plated from ammoniacal solution) surrounded by a small amount of cobalt gave the best results.

The gauze electrodes were next employed. These electrodes were plated with cobalt from both neutral and ammoniacal plating solutions. Again the electrodes plated from ammoniacal solution gave the most satisfactory results. Because the plated cobalt on the gauze was not subject to strain, as is the case of plates on rod electrodes and because with the gauze electrodes the presence of the reduced metallic cobalt was not necessary, it was found more desirable and convenient to use gauze electrodes in the following measurements.

The concentration of the solutions used in the cells was 0.5 N. and 0.1 N.

TABLE IV

Cell No.	Nature of Electrode	Plating Soln.	Conc. $CoSO_4$	Days				
				1	2	3	4	5
1G	plated gauze	Neutral	0.5N	0.901	0.915			
2G				0.895	0.902			
3G	"	"	"	0.904	0.900	0.921	0.917	0.936
4G				0.884	0.901	0.927	0.919	0.935
5G	"	Amm.	"	0.985	0.984	0.985		
6G				0.981	0.984	0.985		
7G	"	"	"	0.975	0.954			
8G				electrode broke after plating				
9G	"	"	"	0.978	0.975	0.975		
10G				0.977	0.976	0.977		

2. Nature of Plating Solution

The conclusion drawn from the above results was that the ammoniacal plating baths were the most satisfactory.

3. Effect of Current Density

From the results listed in Table II, the best deposits seem to be obtained using 0.1 ampere. Payne(33) observed that 0.05 to 0.1 ampere gave the most desirable plate using the same electrodes.

Amperage in excess of the amperages mentioned resulted in large crystalline deposits, especially at the end of the electrodes. A low amperage employed for a longer period of time gave the best results especially with the gauze electrodes.

For the two series of measurements .05 amperes over a period of 18 hours were used.

4. Effect of Cell Electrolyte Solution

In some of the first measurements 0.001 molal sulphuric acid was introduced to prevent hydrolysis of the cobalt sulphate after the method of Murata.(34) However, no perceptible change was noticed in the E.M.F. measurements when the acid was eliminated from the cell electrolyte.

Consequently the cobalt sulphate solutions alone were used for the cell electrolyte in the later measurements.

5. Effect of Time

Experiments with the first cells indicated that after three days the E.M.F. did not change with marked degree. Consequently in the subsequent measurements the cells were measured over a period of at least three days. From the data obtained it was decided that in three days the cells had reached the equilibrium state for there was no marked change in the E.M.F. measurement after that time.

In the second series lack of time prevented measurements being made after three days had elapsed. Consequently the tables were compiled for both series using measurements extending over a period of three days.

6. Effect of Air

The experiments of Randall and Stone(35) prove that the effect of air on the potential of the mercurous sulphate, mercury, electrode is negligible.

In order to determine the effect of air upon the electrode potential of cobalt, two series of cells were measured.

In the one series the solutions used to fill the cobalt, cobalt sulphate, half cell were exposed to air and the cells filled in the usual way. There was no precaution taken to exclude air from the solutions.

The other series, however, were filled by a process according to Haring and Bosche(36) where the air is excluded from the solutions filling the cells.

(a) Procedure

The half cells were carefully cleaned and dried. The mercurous sulphate, mercury, half cell was then prepared. The platinum electrode was amalgamated by electrolyzing a mercurous nitrate solution, then covered with pure mercury.

An amount of the prepared mercurous sulphate, sufficient to form a very thin layer over the mercury was then introduced, and the half cell filled in the usual manner with the cobalt sulphate solution. The half cell with the exception of the side arm was painted black to prevent the light from affecting the mercurous sulphate. The side arm of the mercurous sulphate, mercury, half cell was then introduced into a bridge containing the same concentration of cobalt sulphate solution.

For the first series of measurements the cobalt, cobalt sulphate, half cell was prepared in the following manner; the platinum gauze electrode was plated from an ammoniacal solution of cobalt sulphate using 50 milliamperes of current over a period of 18 hours. The plated electrode was then washed with a solution of cobalt sulphate and then placed in a half cell containing a solution of cobalt sulphate of the same concentration as the wash solution. The side arm of the filled cobalt, cobalt sulphate, half cell was then also introduced into the bridge containing the cobalt sulphate solution of the same concentration.

In the second series of measurements the procedure was identical except in that the filling of the cobalt, cobalt sulphate, half cells was accomplished with the exclusion of air. Haring's(37) method was used.

The completed cells were then placed in the thermostat and the leads to the two-way switch (which was connected to the potentiometer circuit) were inserted in the mercury filled tubes. The cells were allowed to remain in the bath for at least thirty minutes, in order to come to the temperature of the bath. The switch was then closed and readings taken daily for at least three days (time required for cells to reach equilibrium).

Table V lists the measurements of the two series.

(b) Results

TABLE V

Series I

Cell No.	Concentration Approximate Normality	Days				
		1	2	3	4	5
33	0.1	0.9470	0.9503	0.9508		
34		- -	0.8067	0.9161		
35	0.05	0.9404	0.9478	0.9484		
36		0.9321	0.9286	0.9504		
31	0.02	0.9600	0.9521	0.9532	0.9532	
32		0.9442	- -	0.9452	0.9452	
37	0.01	0.8757	0.8791	Discontinued		
38		0.9513	0.9560			
41	0.01	0.9537	0.8887	0.8902	0.8910	0.8900
42		0.9015	0.9114	0.9140	0.9110	0.9098
43	0.005	0.9468	0.9367	0.9357	0.9315	
44		0.9265	0.9184	0.9175	0.9310	
45	0.002	0.8962	0.9000	0.9000		
46		0.8899	0.9000	0.9007		
47	0.001	0.8753	0.8926	0.8836	0.8883	
48		0.8906	0.8845	0.8892	0.8881	
49	0.0005	0.8511	0.8073	0.8713		
50		0.8922	0.9191	0.9588		
51	0.0002	0.9321	0.9275	0.9189		
52		0.9159	1.0019	0.8834		
53	0.0001	0.8426	0.9000	0.9000		
54		0.8000	0.8000	0.8330		

TABLE V
(continued)

Series II

Cell No.	Concentration Approximate Normality	Days 1	2	3	4	5
55	0.1	0.9450	0.9308	0.9325	- -	0.9300
56		0.9103	0.9139	0.9109	- -	0.9100
57	0.05	0.9216	0.9341	0.9235		
58		0.9670	0.9280	0.9282		
59	0.02	0.9240	0.9631	0.9482		
60		0.9486	0.9632	0.9435		
61	0.01	0.9445	0.9370	0.9190		
62		0.9164	0.9438	0.9197		
63	0.005	0.9426	0.9426	0.9362		
64		0.9860	0.9925	0.9913		
65	0.002	0.9650	0.9435	0.9653		
66		0.9742	0.9531	0.9580		
67	0.001	0.9736	0.9677	0.9855		
68		0.9310	0.9182	0.9068		
69	0.0005	0.9876	0.9420	0.9000		
70		0.9226	0.9290	0.9385		
71	0.0002	0.9690	0.9670	0.9156		
72		0.9674	0.9635	0.9710		
73	0.0001	1.0274	0.9345	0.9350		
74		0.9627	0.9535	0.9378		

TABLE VI

Series I

Cell No.	Normality approx.	Density	Normality (exact) (calc. from density)	Molality	log m	E	$\frac{E}{.05915}$ + log m	N	$\sqrt{N}$
33 34	0.1	1.0049	0.1021	0.0512	$\bar{2}$.7095 -1.2905	0.9335	14.78	0.2044	0.4521
35 36	0.05	1.0016	0.0589	0.0295	$\bar{2}$.4702 -1.5298	0.9494	14.52	0.1180	0.3436
31 32	0.02	0.9986	0.0196	0.00985	$\bar{3}$.9934 -2.0066	0.9492	14.11	0.0393	0.1983
41 42	0.01	0.9980	0.0118	0.00589	$\bar{3}$.7703 -2.2297	0.9176	13.29	0.0236	0.1537
43 44	0.005	0.9977	0.00785	0.00394	$\bar{3}$.5955 -2.4045	0.9266	13.25	0.0157	0.1253
45 46	0.002	0.9973	0.00262	0.00131	$\bar{3}$.1179 -2.8821	0.9000	12.34	0.0052	0.0723
47 48	0.001	- -	0.001	0.000501	$\bar{4}$.7001 -3.2999	0.8864	11.69	0.0020	0.0447
51 52	0.0002	- -	0.0002	0.0001	$\bar{4}$.0000	0.9012	11.24	0.0004	0.0200

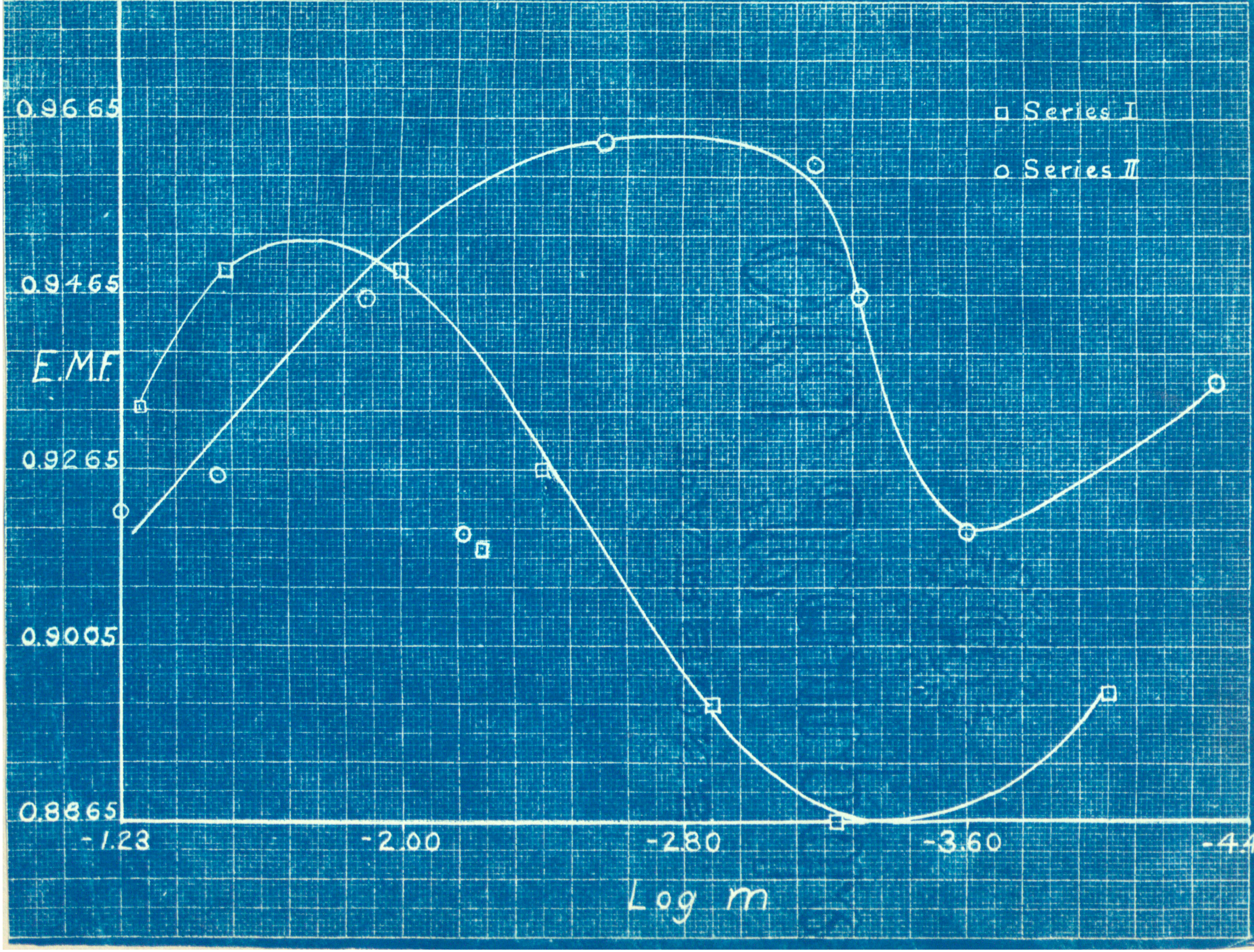
TABLE VI

Series II

Cell No.	Normality approx.	Density	Normality (calc. from density)	Molality	log m	E	$\frac{E}{.05915}$ + log m	N	$\sqrt{N}$
55 56	0.1	1.0060	0.1165	0.05842	$\bar{2}.7665$ -1.2335	0.9217	14.35	0.233	0.4827
57 58	0.05	1.0018	0.0615	0.03084	$\bar{2}.4892$ -1.5108	0.9259	14.14	0.123	0.3508
59 60	0.02	0.9989	0.0236	0.01181	$\bar{2}.0723$ -1.9277	0.9459	14.06	0.0471	0.2171
61 62	0.01	0.9981	0.0131	0.00656	$\bar{3}.8172$ -2.1828	0.9194	13.36	0.0262	0.1618
63 64	0.005	0.9975	0.00524	0.00261	$\bar{3}.4172$ -2.5829	0.9638	13.71	0.0105	0.1024
65 66	0.002	0.9972	0.00131	0.000656	$\bar{4}.8172$ -3.1828	0.9617	13.08	0.00262	0.0512
67 68	0.001	- -	0.001	0.000503	$\bar{4}.7003$ -3.2997	0.9462	12.70	0.002	0.0447
69 70	0.0005	- -	0.0005	0.000251	$\bar{4}.3992$ -3.6008	0.9193	11.93	0.001	0.0316
71 72	0.0002	- -	0.0002	0.000100	$\bar{4}.0013$ -3.9987	- -	- -	- -	- -
73 74	0.0001	- -	0.0001	0.0000502	$\bar{5}.7003$ -4.2997	0.9364	11.53	0.0002	0.0141

Cells number 10 to number 32 inclusive were not included in this series of measurements for the factors in their preparation were not comparable to the cells given in Tables V and VI.

The values of the two cells for each concentration were averaged and plotted as a function of the logarithm of the molalities. The molalities were calculated from the densities of the cell solutions.


0.9665
0.9465
E.M.F.
0.9265
0.9005
0.8865
-1.23
-2.00
-2.80
-3.60
-4.40
Log m
□ Series I
○ Series II

From the above curve the following smoothed values were obtained.

TABLE VII

m mols. $CoSO_4$/1000 gms. H_2O	E.M.F. Series I (with air)	 Series II (without air)
0.05	0.9331	0.9213
.02	.9501	.9378
.01	.9480	.9485
.005	.9325	.9591
.002	.9095	.9656
.001	.9000	.9645
.0005	.8989	.9538
.0002	.8995	.9197
.0001	.9000	.9271

The values obtained with the more concentrated solutions are experimentally more certain.

As in the case of the density determinations the results obtained below the concentration of 0.002 molal were unsatisfactory.

In Series II in which air was excluded from the cell solutions the E.M.F. increased with dilution as it normally should while Series I did not behave in any regular manner. However below the concentration of 0.002 it seems that the E.M.F. values of Series I reached a constant value while in Series II the E.M.F. steadily decreased. The values of Series II at these low concentrations gave higher values than those of Series I.

A visible change in the appearance of the electrode itself was also noted. In the first series the electrodes usually became discolored, attaining a brownish color, after a few days. The electrodes of Series II retained their original color throughout the series of measurements.

For the cell,

$$Co(s),\ CoSO_4(m),\ Hg_2SO_4(s) + Hg(l)$$

the anode reaction is

$$Co(s) + 2\oplus \longrightarrow Co^{++}(f\pm\ m)$$

and

$$E_1 = E_1^o - \frac{RT}{2F} \ln f\pm m$$

while at the cathode;

$$2Hg(l) + SO_4^{--}(f\pm m) + 2\oplus \longrightarrow Hg_2SO_4(s)$$

$$E_2 = E_2^o - \frac{RT}{2F} \ln \frac{1}{f\pm m}$$

Now

$$E = E_1 - E_2$$

and

E was determined experimentally, and substituting values of E_1 and E_2 we have;

$$E = E_1^o - E_2^o - \frac{RT}{2F} \ln f\pm m + \frac{RT}{2F} \ln \frac{1}{f\pm m}$$

Let $E_o^1 = E_1^o - E_2^o$

$$E = E^1_0 - \frac{RT}{2F} \ln(f\pm m)^2$$

$$E = E^1_0 - \frac{RT}{F} \ln f\pm m$$

$$= E^1_0 - \frac{RT}{F} \times 2.303 \log f\pm m$$

$$= E^1_0 - .05915 \log f\pm - .05915 \log m$$

$$\frac{E}{.05915} = \frac{E^1_0}{.05915} - \log f\pm - \log m$$

or

$$\log f\pm - \frac{E^1_0}{.05915} = -\left[\frac{E}{.05915} + \log m\right] \qquad (1)$$

$\frac{E}{.05915} + \log m$ was plotted as a function of $\sqrt{N}$ (ionic strength)

The average straight line was extrapolated to $\sqrt{N} = 0$

Let this value be y (the intercept)

For $\sqrt{N} = 0$ i.e. $m = 0$ and equation (1) becomes

$$0 - \frac{E^1_0}{.05915} = -y$$

whence $E^1_0 = .05915y$

But $E^1_0 = E^0_1 - E^0_2 = 0.05915y$

so that

$$E^0_1 = .05915y + E^0_2$$

where E^0_1 represents the electrode potential of cobalt.

$$E^0_1 = 0.05915y + E^0_2$$

here $y = 14$

$E^0_2 = -0.6213$

$E^0_1 = 0.8281 - 0.6213$

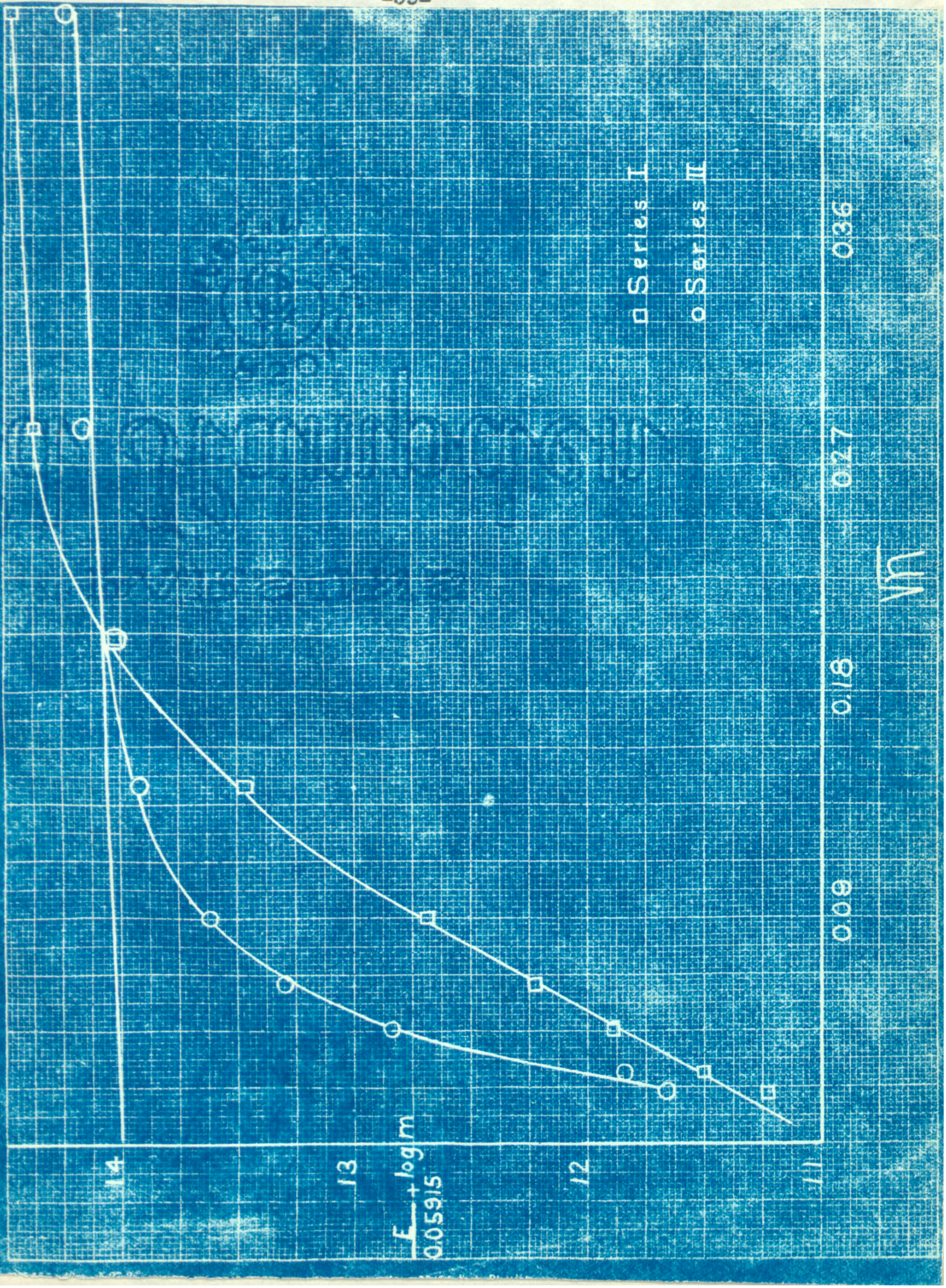
$= +0.2068$ volts for cobalt.

As the second series measurements gave the most satisfactory electromotive force measurements, the results of this series was used for the calculation of the cobalt potential. The electromotive force values in the more dilute solutions were manifestly too low for purposes of calculating the cobalt potential.

TABLE VIII

(data for curve $\frac{E}{0.05915} + \log m$ vs $\sqrt{N}$)

Molality	log m	E Series I	$\frac{E}{0.05915} + \log m$	E Series II	$\frac{E}{0.05915} + \log m$	$\sqrt{N}$
0.05	$\bar{2}.6990$ $-\underline{1}.3010$	0.9331	14.47	0.9213	14.27	0.4472
.02	$\bar{2}.3010$ $-\underline{1}.6990$	.9501	14.36	.9378	14.15	.2829
.01	2.000	.9480	14.03	.9485	14.03	.2000
.005	$\bar{3}.699$ $-\underline{2}.301$	.9325	13.46	.9591	13.91	.1414
.002	3.3010 -2.699	.9095	12.68	.9656	13.62	.0895
.001	-3.000	.9000	12.22	.9645	13.30	.0633
.0005	$\bar{4}.699$ $-\underline{3}.301$	.8989	11.89	.9538	12.83	.0447
.0002	4.3010 -3.699	.8995	11.51	.9197	11.84	.0283
.0001	-4.000	.9000	11.22	.9271	11.67	.0200


$\frac{E}{0.05915} + \log m$
14
13
12
11
0.09
0.18
0.27
0.36
$\sqrt{n}$
□ Series I
○ Series II

7. Effect of Concentration on Potential of Cobalt

The electrode potentials listed in Table I have been determined using in the majority of cases normal cobalt sulphate solutions as the electrolyte. In order to determine the effect of concentration, especially in dilute solution, measurements were made with solutions ranging from 0.05 molal to 0.00005 molal.

The exact concentrations were obtained by determining the densities and calculating the normalities using the formula of Payne.(38) This formula was-found applicable to a concentration of 0.001 molal. The more dilute solutions were prepared by accurately weighing the required amounts of cobalt sulphate.

The electrodes were prepared and measurements made as noted under (a) Procedure.

The results of these measurements are also listed in Table VII. Measurements of the second series were most satisfactory, the electromotive force values increased with dilution.

The change of the electromotive force with the concentration of the solution may be checked by calculating the difference between the electromotive forces of the cells. The following calculations were made assuming that the substances were completely ionized and their ions were perfect solutes.

$$\mathrm{Co(s),CoSO_4(0.02m),Hg_2SO_4(s)\ Hg(l)} \,\Big|\, \mathrm{Hg(l)\ Hg_2SO_4(s),CoSO_4(0.05m),Co(s)}$$

$$-\Delta F = EnF = NRT\ \ln \frac{a_1}{a_2} \quad \overset{\longrightarrow}{\oplus}$$

Electrode reactions:

$$\mathrm{Co(s)} + \cancel{2\oplus} \longrightarrow \mathrm{Co^{++}(0.02m)}$$

$$\mathrm{Hg_2SO_4(s)} \longrightarrow \mathrm{2Hg(l)+SO_4^{--}\ (0.02)} + \cancel{2\oplus}$$

$$\text{(a)}\ \mathrm{Co(s)+Hg_2SO_4(s)} \longrightarrow \mathrm{2Hg(l)+Co^{++}SO_4^{--}(0.02m)}$$

$$\mathrm{2Hg(l)+SO_4^{--}(0.05m)} + \cancel{2\oplus} \rightarrow \mathrm{Hg_2SO_4(s)}$$

$$\mathrm{Co^{++}(0.05m)} \longrightarrow \mathrm{Co(s)} + \cancel{2\oplus}$$

$$\text{(b)}\ \mathrm{2Hg(l)+Co^{++}SO_4^{--}(0.05m)} \longrightarrow \mathrm{Co(s)+Hg_2SO_4(s)}$$

$$\text{(a)}\ \cancel{\mathrm{Co(s)}} + \cancel{\mathrm{Hg_2SO_4(s)}} \rightarrow \cancel{\mathrm{2Hg(l)}} + \mathrm{Co^{++}SO_4^{--}(0.02m)}$$

$$\text{(b)}\ \cancel{\mathrm{2Hg(l)}} + \mathrm{Co^{++}SO_4^{--}(0.05m)} \longrightarrow \cancel{\mathrm{Co(s)}} + \cancel{\mathrm{Hg_2SO_4(s)}}$$

$$\mathrm{Co^{++}SO_4^{--}(0.05m)} \longrightarrow \mathrm{Co^{++}SO_4^{--}(0.02m)}$$

Net result is transfer of 1 $\mathrm{Co^{++}SO_4^{--}}$ as ions from 0.05 molal $\mathrm{CoSO_4}$ to 0.02 molal $\mathrm{CoSO_4}$.

(1) $-\Delta F = NRT\ \ln \frac{(a\pm)_1}{(a\pm)_2} = \frac{0.05}{0.02} = 2.5$

$= 2\mathrm{x}8.316\mathrm{x}298\mathrm{x}2.303\mathrm{x}\log 2.5$

$= 4560$

(2) $-\Delta F = EnF$

$4560 = \Delta E\mathrm{x}2\mathrm{x}96{,}500$

$\Delta E = 0.0236$

TABLE IX Series II

Molality	E.M.F.	ΔE (observed)	ΔE (calculated)
0.05	0.9313		
.02	.9378	0.017	0.024
.01	.9485	0.011	0.018
.005	.9591	0.011	0.018
.002	.9656	0.007	0.024

SUMMARY AND CONCLUSIONS

The following factors affecting the electrode potential of cobalt have been studied; the nature of the electrode, the nature of the plating solution, the effect of current density, the effect of the cell electrolyte solution, the effect of time, the effect of air and the effect of concentration.

It has been shown that the platinum gauze plated with cobalt was the most convenient and reproduceable electrode.

It has been shown that ammoniacal solutions of cobalt sulphate approximately 2.5 normal gave the most satisfactory plate of cobalt.

It has been shown that 0.05 to 0.10 ampere deposited the most satisfactory plate of cobalt.

It has been shown that the introduction of 0.001 molal sulphuric acid into the cell solution had no noticeable effect upon the electromotive force. It has been suggested that hydrolysis has not had time to occur within the time the cells were measured.

It has been shown that the cells came to equilibrium within three days.

The electromotive force of the cell Co(s), $CoSO_4$(m), Hg_2SO_4 + Hg at concentrations .0512 molal to .0001 molal have been measured at 25°C. both in the presence of air and with the exclusion of air.

It has been shown that air has a very marked effect on the electromotive force. The cell solutions from which air was excluded gave the most satisfactory results.

The electrode potential of cobalt has been determined by the extrapolation of the curve, $\frac{E}{0.05915} + \log m$ plotted as a function of $\sqrt{N}$. The value was found to be $+0.2068$ volts.

It has been shown that the change of the electromotive force with the concentration of the solutions is of the same order as the calculated values in the case where air has been excluded from the cell solutions.

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