

UNIVERSITY OF CINCINNATI

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I hereby recommend that the thesis prepared under my supervision by Elmer Curry Payne entitled "The Electrical Transference Numbers of Aqueous Solutions of Cobalt Sulphate." be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

R. L. Cantelo.

W. M. Burgess, Chairman.

THE ELECTRICAL TRANSFERENCE NUMBERS OF AQUEOUS SOLUTIONS
OF
COBALT SULPHATE

A THESIS

Presented to the Faculty
of the
Graduate School
of the
University of Cincinnati

in partial fulfillment of the requirements for the
degree of

Doctor of Philosophy

COBALT
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E. C. Payne

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INTRODUCTION AND THEORY

The electrical transference (or transport) number of an ion-constituent of an electrolyte may be defined as the ratio of the current carried by that ion, to the total current passed through the solution.

$$\text{Thus: } T_c = \frac{F_c}{F} \quad T_a = \frac{F_a}{F}$$

where T_c = transference number of cations

and T_a = transference number of anions

F = total current passed

and $F_c + F_a = F$, where F_c and F_a are the respective fractions of the total current carried by the cation and anion.

This holds only for a binary electrolyte.

The equations for the transference number of an ion in a mixture of electrolytes may be expressed as shown below:

Let there be 2 negative ions, A_1 and A_2 , and 2 positive ions, C_1 and C_2 . Let the number of equivalents transferred to the cathode be N_{A_1} , N_{A_2} , N_{C_1} , N_{C_2} . Then the transference number of the cation C_1 , will be given by the expression:

$$T_{C_1} = \frac{N_{C_1}}{N_{C_1} + N_{C_2} - N_{A_1} - N_{A_2}} = \frac{N_{C_1}}{\sum N_C - \sum N_A}$$

Therefore, the transference number of an ion-constituent equals the number of equivalents transferred by 1 Faraday of electricity. (Here $\sum N_C - \sum N_A = 1$).

(Note): (This treatment is due to Noyes and Falk.⁽¹⁾)

Since, by Faraday's law, all ions are discharged at a rate depending only on their respective charges, and since the phenomenon of transference implies that some ions move faster than others, it might seem that there would be an accumulation of the faster ions around the pole to which they are attracted, causing this solution to be charged, and leaving the solution around the other pole oppositely charged.

Although this may be true to some slight extent and cause some of the electrode phenomena, by far the greater part of these transferred ions are associated with an equivalent number of the oppositely charged ions: that is; the solution is neutral.

That this must be true may be seen from Ostwald's diagram, which is usually included in all text-books of physical chemistry. In it the ions are considered as being aligned in rows, alternately positive and negative. These rows slip past one another when a current is passed through; the row of faster-moving ions being further displaced. Thus the excess of positive or negative ions which has moved into the vicinity of a given electrode, is always associated with

an equivalent number of oppositely charged ions which have failed to move away.

Thus the change in concentration of the electrolyte about an electrode is a measure of the transference of its ion-constituents.

Transference, then, denotes the removal of a quantity of electrolyte from the vicinity of one electrode, and the placing of it in the vicinity of the opposite electrode.

We may express transference numbers as follows:

$$T_C = \frac{N_C}{N_C + N_A} = \frac{N_C}{N}$$

$$T_A = \frac{N_A}{N_C + N_A} = \frac{N_A}{N} \quad \text{where}$$

T_C = transference number of cations

T_A = transference number of anions

N_C = number of equivalents of cation transferred to the vicinity of the cathode.

N_A = number of equivalents of anion transferred to the vicinity of the anode.

N = total number of Faradays passed.

From the above considerations it is evident that the transference number of an ion is a measure of its velocity, and may be expressed as a function of the velocities of the two ions.

The quantity N of a given ion transferred is equal to: Cross-section area (a) x equivalent concentration of this

ion (Z) x time (t) x velocity of this ion (U).

$$N = atUZ$$

(N and U are negative for negative ions if transference toward the cathode is called positive.)

Therefore, the transference number of the cation C_1 is T_{C_1} and is given by:

$$T_{C_1} = \frac{U_{C_1} Z_{C_1}}{(U_{C_1} Z_{C_1} + U_{C_2} Z_{C_2} + \dots - U_{A_1} Z_{A_1} - U_{A_2} Z_{A_2} - \dots)}$$

$$= \frac{U_{C_1} Z_{C_1}}{\sum U_{C_1} Z_{C_1} - \sum U_{C_2} Z_{C_2}}$$

For an electrolyte with only 2 species of ions, this reduces to:

$$T_C = \frac{U_C}{U_C + U_A} \quad \text{and} \quad T_A = \frac{U_A}{U_C + U_A}$$

Transference numbers may also be expressed as functions of conductance.

The equivalent conductance, Λ , of a solution of an electrolyte is defined as being equal to the sum of the ion-conductances of its constituent ions. $\Lambda = \Lambda_{A^+} + \Lambda_C$

Now, since the ion conductances are dependent on the speed of the respective ions, transference numbers may be expressed thus:

$$T_C = \frac{\Lambda_C}{\Lambda_C + \Lambda_A} \quad \text{and} \quad T_A = \frac{\Lambda_A}{\Lambda_C + \Lambda_A}$$

(Note): (For further discussion of conductance, and especially for that of cobalt sulphate solutions, see A. J. Berger⁽²⁾.)

There have been, in general, three distinct methods for determining transference numbers, viz:

(1) The Hittorf Method, (2) The Moving-Boundary Method, and (3) Calculations from measurements of the E.M.F. of concentration cells.

The Moving-Boundary Method measures the absolute distance moved by the ions, by means of observing the displacement of the boundaries between the solution containing the electrolyte to be measured, and two other solutions, each having one ion in common with the given solution. From these data the transference numbers may be calculated from the equation given previously. This method was first suggested by Lodge⁽³⁾. This method is not applicable, with any degree of accuracy, to solutions of bi-bi-valent electrolytes. (cf. Noyes and Falk⁽¹⁾.)

For this thesis problem the Hittorf method was used. In this method the transference numbers are calculated from the changes in concentration of the solution about the electrodes. The total amount of electrolyte transferred may be thus found and thence the transference numbers calculated, with the aid of the equations previously shown.

It is hoped that the results of this investigation may be checked later, by comparison with results calculated from the E.M.F. of concentration cells.

The following is the equation for the E.M.F. of such a cell:

$$E_t = \frac{2N_C RT}{nF} \ln \frac{C_2}{C_1}$$

where E_t = E.M.F. of the cell

N_C = transference number of cations

C_2 & C_1 = concentrations

F = 1 Faraday

n = number of Faradays

Now if E_t is measured and C_2 and C_1 are known, N_C may be calculated. Or, since the E.M.F. of a cell without transference is:

$$E = \frac{2RT}{nF} \ln \frac{C_2}{C_1}$$

we may divide the first equation by the second and obtain:

$$N_C = \frac{E_t}{E}$$

Thus if we measure the E.M.F. of a similar cell, without transference, we can calculate the transference numbers by this equation.

Since it had been postulated that ions may be hydrated, Nernst⁽⁴⁾ suggested the use of an inert material, such as sugar, as a reference material. If this material does not move, the ionic hydration may be calculated, and the transference numbers corrected.

This idea has been investigated by Reinhold⁽⁵⁾;

Büchböck⁽⁶⁾, and especially by Washburn⁽⁷⁾.

Washburn calls these corrected values "true" transference numbers. However, in this investigation, no attempt was made to determine ionic hydration, and consequently the values given represent Hittorf numbers, and not "true" or corrected transference numbers.

These corrected values may be calculated, with the use of an inert reference material, if the amounts of solvent associated with a given weight of this reference substance, before and after electrolysis, are known. Thus if

T_A = "True" transference number

T = Hittorf number

ΔN_0 = moles of solvent transferred to cathode per Faraday

N = equivalents of electrolyte in solution associated with N_0 mols of solvent

$$T_A = T \left(1 - \frac{\Delta N_0 N}{N_0} \right)$$

If N = number equivalents electrolyte associated with 1000 gms., or 55.5 moles of water, this reduces to:

$$T_A = T \left(1 - .018N \Delta N_0 \right)$$

The amount of solvent transferred to cathode = amount carried to it by positive ions, minus that carried away by negative ions.

HISTORICAL

The first noteworthy investigation of transference numbers was made by Hittorf⁽⁸⁾.

Previously Gmelin,⁽⁹⁾ Daniell and Miller,⁽¹⁰⁾ and others, had observed that an unequal transference occurs when a current passes through the solution of an electrolyte, but their results were not definite nor quantitative.

Hittorf performed a very large number of experiments with various electrolytes and gave definite values to the ratios of current to transference.

This transference he explained as due to unequal velocities of the ions, and hence to the unequal amounts of current carried by each of them. The "transference number" was then defined as has been shown before.

Among the more notable of recent workers in this field are: A. A. Noyes,⁽¹⁾ Falk,⁽¹⁾ Washburn,⁽⁷⁾ Grinnell Jones,⁽¹¹⁾ McBain,⁽¹²⁾ and others.

Bibliographies of work on transference numbers have been compiled by McBain,⁽¹³⁾ (up to 1905), and by Noyes and Falk⁽¹⁾. (1905-11). The latter give a critical discussion of the values found by various investigators, and have tried to evaluate their relative worth. They have also discussed various experimental methods and attempted to point out the limitations of each, and to give precautions and standards to be followed.

No mention of any determination of the transference numbers in cobalt sulphate solutions was found by the author in the literature.

The only such works on cobalt salts were those of Bein⁽¹⁴⁾ on CoCl_2 , and of Denham⁽¹⁵⁾ on CoBr_2 . Bein gives only one value, viz:

<u>Concentration</u> (as % Cl in soln.)	<u>T_{Cl^-}</u>
0.199%	.596

Denham's results are given in the table below. They show how the values for $T_{\text{Co}}^{\text{++}}$ steadily decrease with increasing concentration, until an apparent negative transference for cobalt is obtained.

TABLE I
 CoBr_2 Solutions (Denham⁽¹⁵⁾)

<u>Concentration</u> (Gm. Mols/L)	<u>$T_{\text{Co}}^{\text{++}}$</u>
.090	+ .409
.459	+ .413
1.345	+ .340
2.448	+ .322
3.106	+ .215
4.731	+ .005
5.554	- .444

Data of Denham (15)

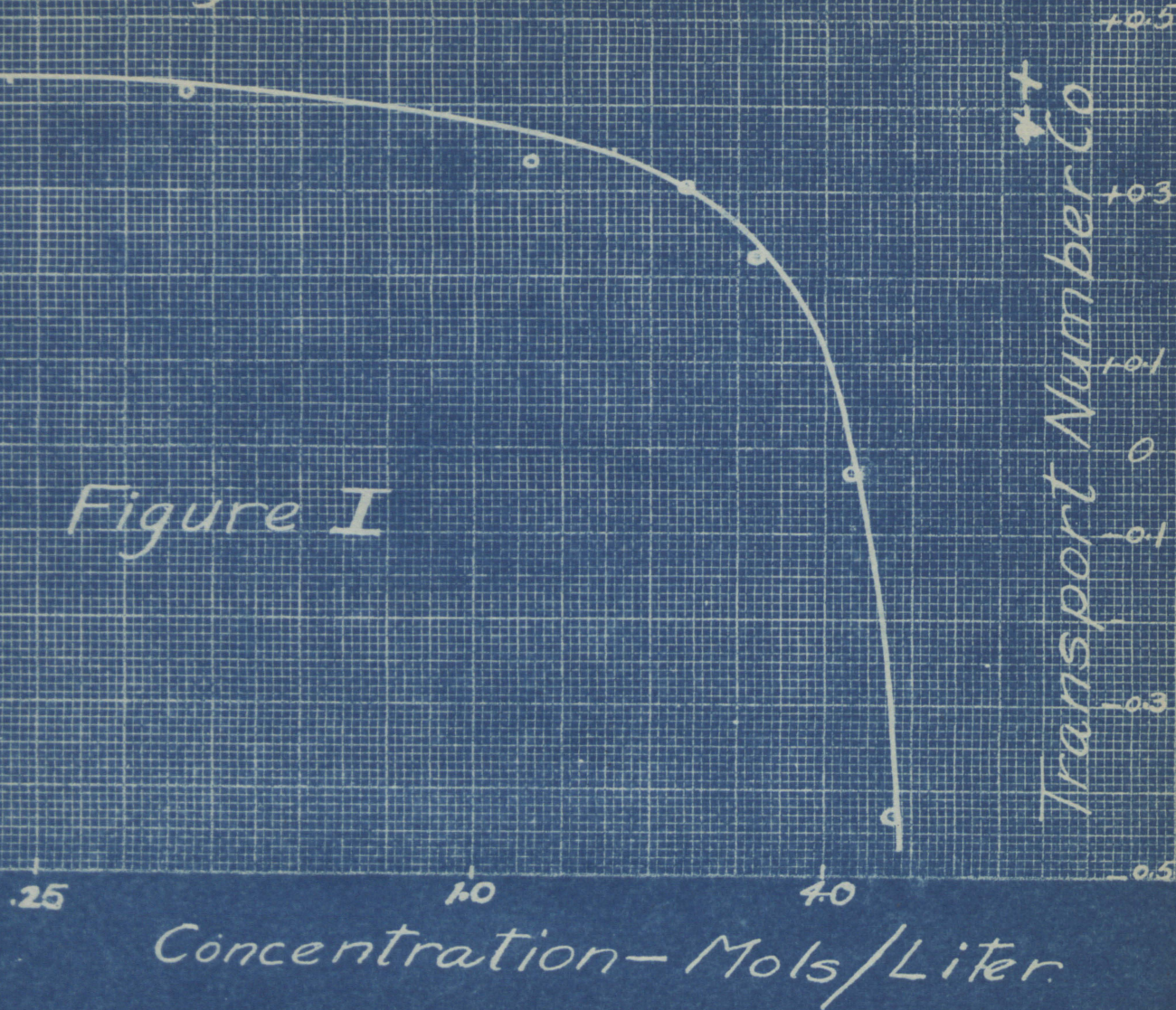


Figure I

FIG. 1

Fig I

Denham explained these decreasing and negative values by assuming the formation of so-called "auto-complexes" such as CoBr_3 and CoBr_4 , which would transfer cobalt toward the anode.

Concerning this kind of phenomena, McBain and Van Rysselberge⁽¹²⁾ have shown that a common anion, when added in large excess, to the solution of a bivalent cation, (and to less extent with univalent cations), will suppress the movement of that ion toward the cathode, and may even reverse its direction, causing it to show a negative transference. Among other salts they have used Li_2SO_4 and MgSO_4 . The behavior of CdI_2 in this regard is well known. It is

supposed to form the complex anion, $\text{Cd}\bar{\text{I}}_3$. Davies⁽¹⁶⁾ has shown how the composition of the complex ions may be calculated with the aid of transference data, if the mobilities or ion-conductances of the simple ions and their activities are known. Thus, in HF solutions he calculates the complex to be $(\text{HF}\bar{2})$.

McBain and Van Rysselberge have shown that these phenomena likewise occur with very concentrated solutions of a single salt. They say:

"If complexes occur in mixtures of two salts, they must also occur in solutions of one salt of the same (anion) concentration. From the mass action principle, even greater amounts of the complexes will be formed, but less in proportion to the total salt present."

They have attempted to show that these results are "incompatible with any complete dissociation theory", since they believe it to be necessary, for complex formation, that the simple anion combine with the undissociated molecule to form the complex ion. Thus: $\bar{\text{I}} + (\text{CdI}_2) \rightarrow (\text{Cd}\bar{\text{I}}_3)$.

OBJECT

The object of this research was to determine the electrical transference numbers of cobalt sulphate solutions, and to determine the effect of changing concentration on these numbers.

EXPERIMENTAL

Purification of Cobalt Sulphate

The cobalt sulphate used was the so-called C.P. grade, and originally contained about 1% nickel, as nickel sulphate.

It was purified in two ways, both of which gave an apparently pure product. However, the first method was better known to be reliable and was used for most of the work.

The First Method:

This is the method used by A. J. Berger,⁽²⁾ and described by Biltz and Biltz⁽²²⁾. Chloro-pentammine cobalti-chloride was thus prepared. This was thoroughly washed with hydrochloric acid 1:1, and then with more dilute acid. It was then dissolved in 2% ammonia solution and reprecipitated with strong HCl, and again washed with 1:1 HCl. The compound was then heated with sulphuric acid, to decompose the ammine and to convert the chloride to the sulphate. The excess H_2SO_4 was vaporized, and the salt heated to $400^\circ C$. It was then dissolved in distilled water, filtered, and finally precipitated from an almost saturated solution by the addition of ethyl alcohol. The precipitate was filtered and washed with a 50-50 mixture of alcohol and water, and again dehydrated and heated to $400^\circ C$. It was then recrystallized from conductivity water.

The salt now gave no test for nickel according to the method described by Murray⁽²³⁾. Analysis of the carefully dehydrated sulphate showed the salt to be pure, within the limits of analytical error.

The Second Method:

This method is that described in "U. S. Bureau of Mines Information Circular 6331".

The cobalt was precipitated from a 5% solution of the sulphate by a solution of sodium hypochlorite containing excess alkali. Precipitation was stopped while the solution was still somewhat pink. The cobalt is precipitated as the greenish-black $\text{Co}(\text{OH})_3$, while the nickel is not precipitated. The solution was decanted off, and the precipitate washed free from chlorides by decantation. This method gave a product which was apparently pure, but the details of the process will bear further attention.

Preparation of Solutions

Conductivity water was used in the preparation of all solutions. It was prepared as follows:

Apparatus was set up as for ordinary steam distillation, with the following specifications: The two flasks were of pyrex glass, round-bottomed, and of 4 liters capacity. The condenser was of block tin. The receiving vessel was of pyrex glass, well steamed and "aged". The water was distilled

from a very dilute alkaline solution of KMnO_4 . No attempt was made to exclude atmospheric CO_2 . The water had a specific conductivity of less than 2.0×10^{-6} reciprocal ohms. Other than that, no special precautions were taken.

The solutions were made up fresh for each determination; well steamed vessels being used.

Analytical Method

All analyses were made by the electrolytic method. Some checks were made by precipitation as phosphate, and ignition to pyrophosphate, and also by precipitating the sulphate as BaSO_4 . However, the electrolytic method was more satisfactory.

Several attempts were made to determine CoSO_4 by direct weighing of the anhydrous salt, but due to the following circumstances, the method was abandoned.

The anhydrous sulphate is either hygroscopic or else it adsorbs water on the surface. At any event it cannot be weighed in an open vessel.

To completely dehydrate the salt in a reasonable time requires a rather high temperature, and, unless carefully regulated, some of the salt was decomposed to the oxide. So, lacking a suitable closed vessel, and suitable temperature control, the method was abandoned.

The electrolytic method was based on that of Lindell and Hoffmann,⁽¹⁷⁾ and was similar to that used by A. J. Berger⁽²⁾.

However, certain modifications were used.

A portion of solution was used which would contain from 0.15 to 0.25 gms. of cobalt. To this was added a mixed solution containing the equivalent of 10 cc concentrated H_2SO_4 , and 55 cc of strong ammonia. The solution was made up to 150 cc, and was electrolyzed for $1\frac{1}{2}$ hours, with a current of 0.6 to 1.0 amperes and a voltage of 2.5 to 3.5. A cylindrical cathode of platinum gauze and a rotating anode consisting of a platinum spiral were used. At the end of one hour, or when the solution became colorless, the cover glass and sides of the beaker were washed down, and about 0.5 gm. $NaHSO_3$ added. The $NaHSO_3$ apparently aids in the deposition of the last portion of cobalt, but tends to form small amounts of sulphide on the cathode. It was not added in all cases, and fairly good checks were obtained between the two methods. If it is not used, the solution must be electrolyzed longer and there is danger of platinum being deposited, as shown later.

Since, as explained later, it was inadvisable to remove all of the cobalt by electrolysis, the residue was precipitated by $(NH_4)_2S$, after boiling off the excess ammonia. The cobalt sulphide was filtered, washed with water containing NH_4Cl and $(NH_4)_2S$, ignited to the oxide, and weighed. This weight, seldom more than 1 milligram, was multiplied by an empirical factor of $\frac{3}{4}$ and the result (as Co) added to the weight of cobalt deposited on the cathode.

At first, considerable difficulty was experienced with this method, and some time was spent studying and standardizing it.

The following precautions were found necessary:

- (1) The electrode should be washed with water and dried at 105°C.
- (2) The solution, before electrolysis should be nearly cold, otherwise the cathode deposit is unsatisfactory.
- (3) The solution should not be electrolyzed too long, or platinum may be plated onto the cathode. Some experiments were performed with the solution as used for analysis, but without any cobalt present, which showed that platinum is dissolved from the anode and some may be plated on the cathode. The table below gives a few of these results.

<u>NaHSO₃ Present?</u>	<u>Volts</u>	<u>Amps.</u>	<u>Time Hrs.</u>	<u>Anode Loss</u>	<u>Cathode Gain</u>
Yes	1.5	0.3	3.0	.0303 g.	.0103 g.
No	"	"	"	.0073	.0000
Yes	"	"	"	.0087	.0002
No	"	"	"	.0223	.0159
No	"	"	"	.0334	.0001

These results show that the conditions for the deposit of platinum were not determined. However, the following was noted:

That when a very pure platinum anode was used, much less was dissolved from it.

That, although appreciable amounts of platinum did dissolve from the anode, very little, if any, was deposited on the cathode until the concentration of cobalt became very low. Hence if the electrolysis was stopped after 1½ to not more

than 2 hours, no measurable amount of platinum was plated out. (See A. J. Berger⁽²⁾, P. 26-27.)

(Notes): (1. The platinum, which dissolved off the anode, apparently did not interfere with the determination of the residual cobalt by precipitation as CoS. This was due, perhaps, to the formation of soluble ammonia complexes, since platinum could be found in the filtrate.

2. All volumetric apparatus used was calibrated at 25°C.)

Density of CoSO₄ Solutions

Since the measurement of solutions for analysis was by volume, it was necessary to know the densities of the solutions.

The solutions were weighed in a density bottle, or pycnometer, of 25 cc capacity, fitted with a ground glass stopper, which was pierced by a capillary. It had no side-arm and was not fitted with a thermometer. It was calibrated by weighing full of water at 25°C., and the capacity found by dividing the weight by the density of water at 25°/4°, which is 0.99707 grams per cc.

Therefore the densities, as determined, represent those of the solutions at 25°C., referred to water at 4°C.

The following was the procedure:

The pycnometer was filled with the solution at a temperature slightly below 25°C, and the stopper inserted.

It was then placed in a widemouth flask sunk into the water bath at 25°C. It was allowed to remain for 20 minutes until it had come to the temperature of the bath. Then the excess, which had overflowed through the capillary was quickly wiped off and the bottle placed in a cool place so that there would be no loss in weight, due to forcing some of the solution through the capillary by expansion. It was then weighed.

The solutions were analyzed by the electrolytic method.

Apparently no one had previously determined the densities of CoSO₄ solutions over an extended range of concentrations. The values found in the literature for 25° are given here.

TABLE II

Density of CoSO₄ Solutions

Data of Charpy (18).		
	<u>Concentration</u> (Equiv. per Liter)	<u>Density</u> (Gms. per cc)
Temp. 25°/4°	.125	1.0080
	.250	1.0163
	.500	1.0353
	1.000	1.0718

Data of Wagner (19).		
Temp. 25°/?	.125	1.0110
	.250	1.0193
	.500	1.0383
	1.000	1.0750

than 3 hours, no measurable amount of platinum was plated out. (See A. J. Berger⁽²⁾, P. 26-27.)

(Notes): (1. The platinum, which dissolved off the anode, apparently did not interfere with the determination of the residual cobalt by precipitation as CoS. This was due, perhaps, to the formation of soluble ammonia complexes, since platinum could be found in the filtrate.

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The pycnometer was filled with the solution at a temperature slightly below 25°C, and the stopper inserted.

It was then placed in a widemouth flask sunk into the water bath at 25°C. It was allowed to remain for 20 minutes until it had come to the temperature of the bath. Then the excess, which had overflowed through the capillary was quickly wiped off and the bottle placed in a cool place so that there would be no loss in weight, due to forcing some of the solution through the capillary by expansion. It was then weighed.

The solutions were analyzed by the electrolytic method.

Apparently no one had previously determined the densities of CoSO_4 solutions over an extended range of concentrations. The values found in the literature for 25° are given here.

TABLE II

Density of CoSO_4 Solutions

Data of Charpy (18).		
	<u>Concentration</u> (Equiv. per Liter)	<u>Density</u> (Gms. per cc)
Temp. 25°/4°	.125	1.0080
	.250	1.0163
	.500	1.0353
	1.000	1.0718

Data of Wagner (19).		
Temp. 25°/?	.125	1.0110
	.250	1.0193
	.500	1.0383
	1.000	1.0750

TABLE II (Continued)

Density of CoSO₄ Solutions

 From International Critical Tables (20).

	Conc. (Equiv. per Liter) (N. Calc. by Author)	<u>Density</u> (Gms. per cc)
Temp. 25°/4°	.130	1.007
	.262	1.017
	.536	1.038
	.819	1.058
	1.115	1.080

 Data of Berger(2)

	<u>Concentration</u> (Equiv. per Liter)	<u>Density</u> (Gms. per cc)
Temp. 25°/25°	0.5	1.0380
	0.2	1.0158
	0.1	1.0079
	.05	1.0040
	.02	1.0020
	.01	1.0009
	.005	1.0004
	.002	1.0000
	.001	1.-----

 The table of densities, as determined by the author,
 is given below:

TABLE III

Density of CoSO₄ Solutions

	<u>Concentration</u> (Equiv. per Liter)	<u>Density</u> (Gms. per cc)
Temp. 25°/ 4°	4.674	1.3340
	4.446	1.3175
	4.370	1.3152
	3.934	1.2834
	3.888	1.2783
	3.354	1.2414
	3.103	1.2243
	2.844	1.2049

TABLE III (Continued)

Density of CoSO₄ Solutions

	<u>Concentration</u> (Equiv. per Liter)	<u>Density</u> (Gms. per cc)
Temp. 25°/4°	2.730	1.1975
	2.498	1.1817
	2.101	1.1524
	1.743	1.1295
	1.586	1.1143
	1.307	1.0967
	1.141	1.0824
	1.094	1.0789
	1.064	1.0776
	0.966	1.0708
	0.842	1.0615
	0.731	1.0528
	0.659	1.0482
	0.496	1.0351
	0.488	1.0342
	0.386	1.0263
	0.249	1.0166
	0.240	1.0157
	0.193	1.0120
	0.118	1.0060
0.101	1.0049	
0.097	1.0046	
0.0499	1.0010	
0.020	0.9985	
0.---	0.9971	

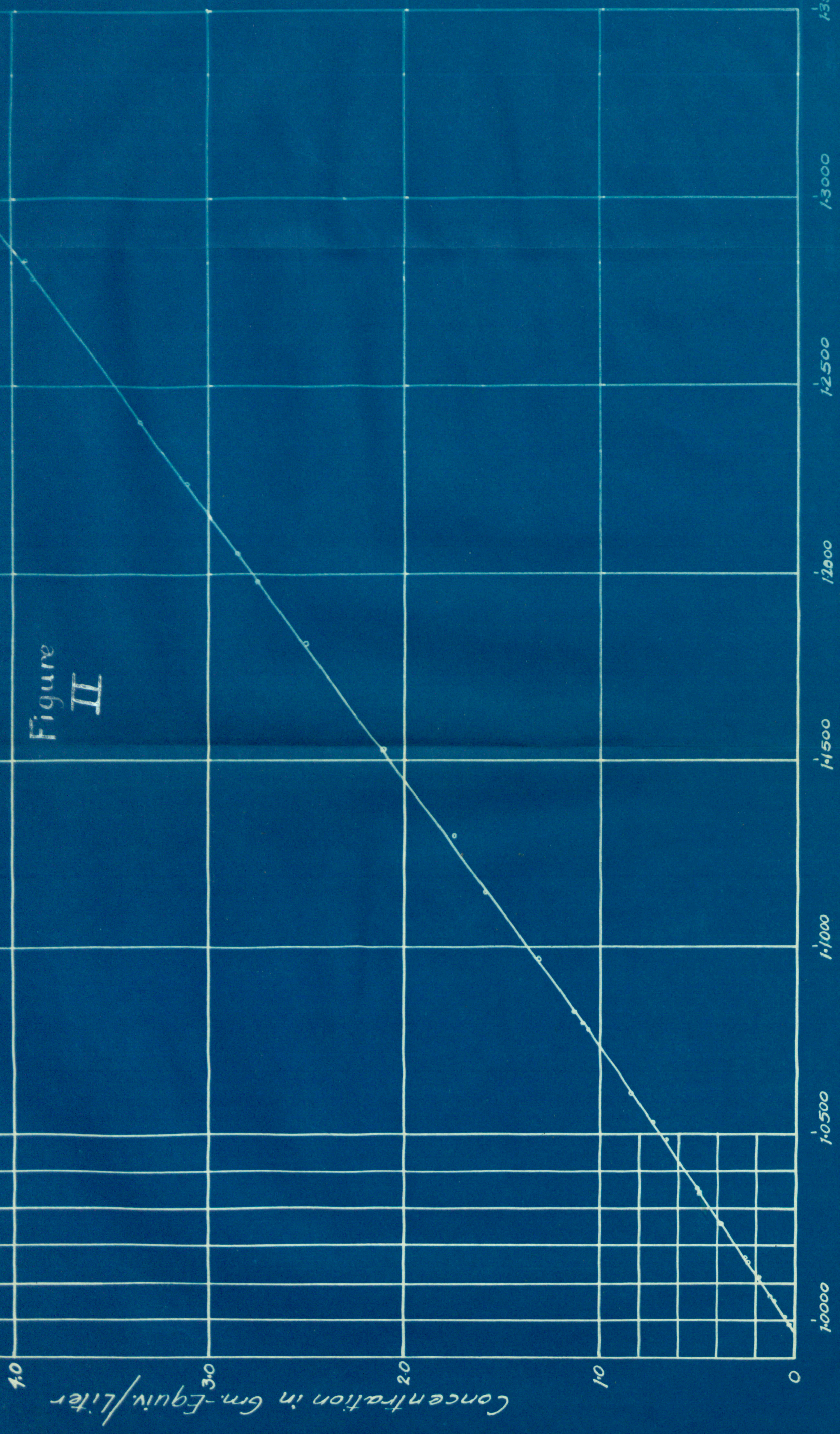


Figure II

Temp. 25°C/4°

Density of CoSO₄ Solutions

Density as Gms./cc.

1.000 1.050 1.100 1.150 1.200 1.250 1.300 1.350

The densities were plotted on coordinate paper as a function of concentration. The curve was extrapolated from a concentration of .02N. to zero. It is linear, or very nearly so, up to a concentration of about 1.1 Normal. Here there occurs a break in the curve and from thence the slope is greater, although it is nearly linear for some distance and breaking upward at the upper end.

The last value, 4.674N., represents a very nearly saturated solution at 25°C.

The equation for the lower part of the curve (up to 1N.) is: $D = 0.9971 + .0764N.$, where D = Density and N. = Normality.

The break in the curve at a concentration of 1.1 Normal is difficult to interpret theoretically, occurring as it does at a concentration of 1CoSO_4 to $100\text{H}_2\text{O}$.

Determination of Transference Numbers

The author has attempted to follow the suggestions of Noyes and Falk⁽¹⁾ in their discussion of methods of determining transference numbers, viz:

1. "Both cathode and anode portions should be analyzed."
(This was done but the anode portion could not be relied upon.)
2. "The change in concentration should be as large as possible."

3. "It is advisable to analyze three middle portions."
(This was done.)
4. "The character of the electrodes should be such as to form no migrating substance likely to cause error in analysis."
5. "Apparatus should be so designed as not to cause convection currents and stirring, during electrolysis and removal of the solution." (Mixing was apparently avoided.)

Apparatus

The apparatus was essentially that of A. A. Noyes⁽²¹⁾. It is shown in Figure III. The inside diameter was 23 m.m. and was uniform throughout. The total distance between the electrodes was about 70 cm. The apparatus was made in two parts, and joined at the middle by rubber tubing, wired tight, and coated with ceresine wax.

Several electrodes were tried, but the only satisfactory ones were: a cathode of very fine platinum gauze; and an anode of similar material, plated with cobalt. These electrodes were flat pieces of gauze about $1\frac{1}{2}$ cm. in diameter. They were welded to pieces of platinum wire, which was sealed into the end of a 6 cm. length of 4 m.m. glass tubing. On the inside of the tube contact was made with a copper wire by means of Wood's metal. This tube, holding the electrode, was joined to a longer one by means of rubber tubing, and the

longer one was held in place at the top of the transference apparatus by passing through a rubber stopper. Electrical contact was made by means of a copper wire passing through the long tube and connected to the wire in the short one by means of a loop and hook.

The electrode end, then, could be detached and weighed.

The first electrodes were of platinum foil, but were discarded since the cobalt would not adhere well to the cathode and cobalt oxide formed on the anode, and fell as a sludge to the bottom of the apparatus. The coat on the anode was, at first, beautiful and iridescent. Its composition was not determined.

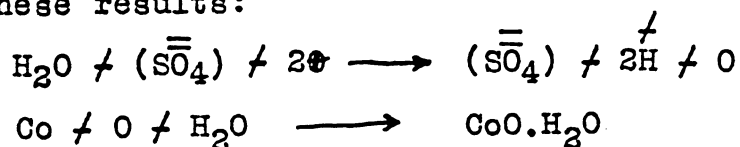
It was then decided to use a cobalt anode, and various materials were plated with cobalt for use as anodes. Among these were spirals of nickel wire and platinum foil. They were all unsatisfactory due to the inability to plate on them enough cobalt in a pure and suitable form.

The gauze electrodes worked much better. The cathode left nothing to be desired. The number of equivalents of cobalt plated on it checked very well with the amount calculated from the silver coulometer.

The best solution for plating the anode was found to be a solution of pure CoSO_4 , at a concentration of 2 Normal, or stronger. It was plated with a current of .05 to 0.1 amperes.

This method gave a gray or shiny adherent plate which was much better than was obtained with ammoniacal solutions.

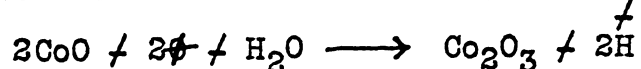
The anode, even with the precautions observed, did not dissolve, on electrolysis, with any degree of regularity, and consequently few of the anode portions of solution could be checked against the cathode portion. The anode generally lost more than would be expected from the amount of current passed. After electrolysis, it was coated with a material which was apparently an oxide and of color varying from pink, blue or green, to brown or black. Some of this material fell to the bottom as a sludge. It was also noted that the solution around the anode gained less cobalt than that around the cathode lost. The following hypothetical reactions could account for these results:



Note: (There are two hydroxides, or hydrated oxides, corresponding to the formula $\text{CoO} \cdot \text{H}_2\text{O}$. One is pink and the other blue. The oxide CoO is brown, Co_2O_3 is gray, and Co_3O_4 is black.)

Thus if an oxide of cobalt was formed and some of it fell off as sludge, there would be less cobalt than might be expected in solution, while the anode might lose more weight than would be accounted for by simple electrolytic solution of cobalt. There might also be some oxidation of

cobalt to the cobaltic condition. Thus:



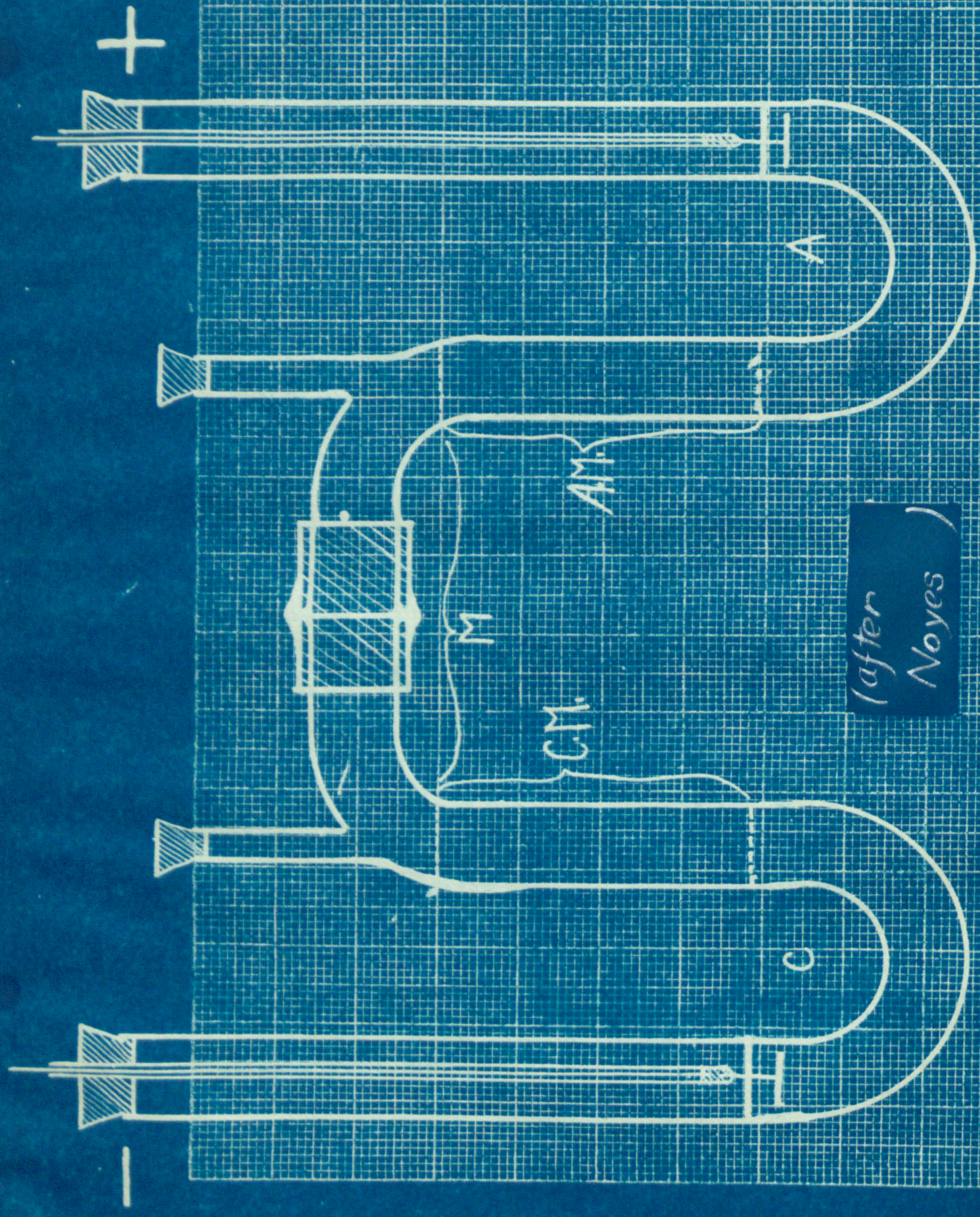
The above considerations are purely hypothetical and no time was spent in detailed investigation. If the concentration of the H^+ ion were found to have increased in the anode portion, the above hypotheses would be strengthened.

Current was measured with a silver coulometer, which was constructed as follows:

The cathode was a deep, platinum dish of about 200 cc capacity. The anode was a bar of pure silver, coated with electrolytic silver. It was wrapped in "ashless" filter paper to prevent the dropping off of sludge. The electrolyte was a 15% solution of silver nitrate. The silver nitrate was purified according to the method of Rosa and Vinal⁽²⁴⁾.

Current was indicated roughly by a milliammeter. The amount of current was adjusted by means of a slide wire resistance.

A water constant temperature bath was used. It was maintained at a temperature of 25.0 ± 0.02 by means of a toluene bulb-mercury gas regulator which operated a micro-gas burner. (See Berger⁽³⁾, p. 51). Cooling water was run through a copper coil, and the bath was stirred with a low speed motor.



(after
Noyes)

Transference Apparatus
Fig. III

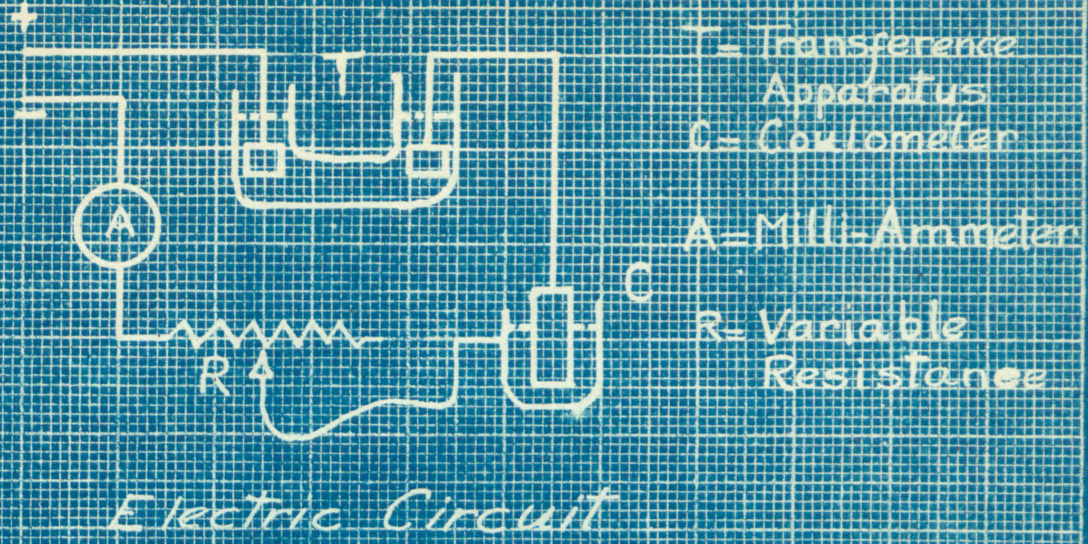
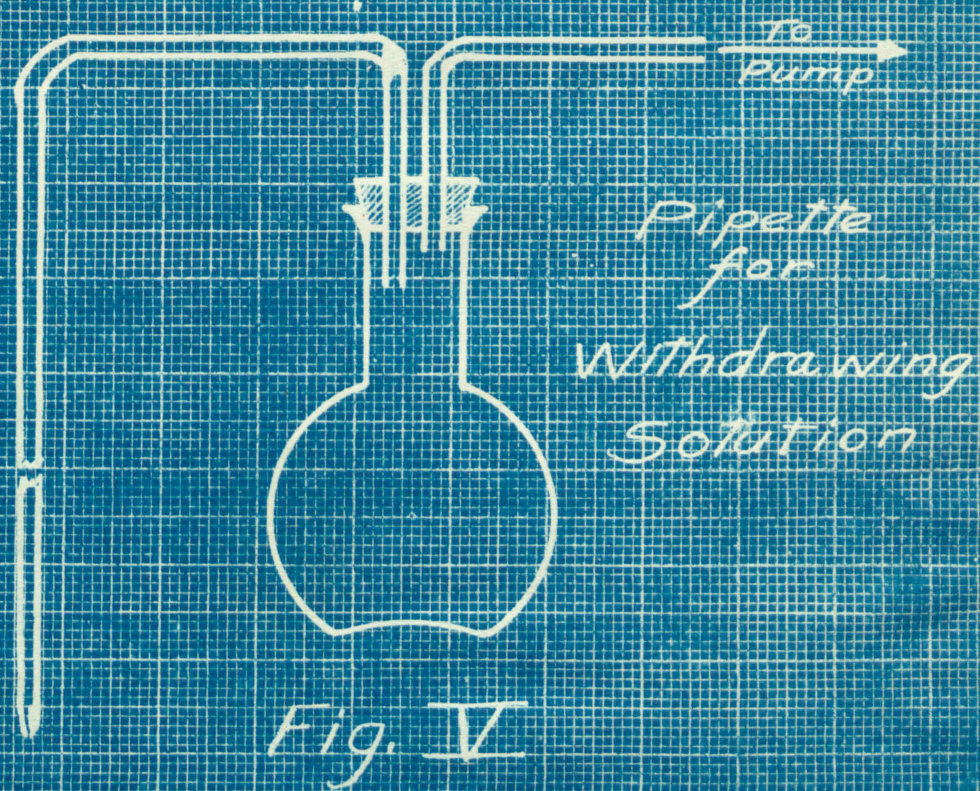


Fig. IV



Procedure

The two halves of the apparatus were carefully cleaned and dried. They were joined, as described previously, and the solution poured into the completed cell.

The levels were adjusted to about 3-4 cm. above the bends in the outer arms, and the small "withdrawal" tubes stoppered.

The electrodes were then inserted, and adjusted so as to be just below the surface of the solution. (The anode had been previously weighed.)

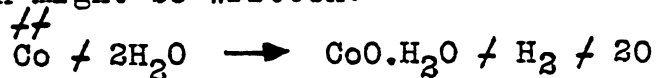
The apparatus was then immersed in the bath, almost to the top of the withdrawal tubes. It was allowed to remain in the bath for at least 30 minutes, in order to come to the bath temperature. Then the current was applied. A sufficiently high potential was used to pass the desired current of 5 to 60 milliamperes, according to the concentration of the solution. Since storage cells were used as a source of electricity, the current could be maintained very constant.

It was passed through for as long a time as, as found by experience, would give a maximum change in concentration about the electrodes, without changing the concentration of the middle portions, and without causing disconcerting electrode phenomena. This time varied from 3 to 12 hours, with 4 to 6 hours as the most usual.

Note: (When the current had passed too long and the solution

around the cathode had become very dilute, a sharp boundary was observed below the cathode, separating the diluted solution from the rest of the solution. The deposit on the cathode became loose, and finally a blue, gelatinous precipitate appeared, holding suspended in it small, bright spangles of metal. This precipitate was thought to be the blue hydroxide, or hydrated oxide, $\text{CoO} \cdot \text{H}_2\text{O}$. Gas bubbles (probably hydrogen) appeared on the electrode surface.

Such a reaction might be written:



Bein⁽¹⁴⁾ noticed similar phenomena with CoCl_2 solution and gave a similar explanation.)

After the current was stopped, the solution was separated into 5 parts. The middle portion (M), and the two adjacent portions, (AM and CM), in vertical arms of the tube, were carefully pipetted directly into dried and weighed flasks, by means of suction. The tip of the pipette was kept just below the surface of the solution to prevent stirring. (See Fig. V)

The two electrodes were then removed and carefully rinsed with a very small amount of the original solution, into their respective compartments.

They were then rinsed with water, dried and weighed. The cathode deposit was dissolved in nitric acid and again dried and weighed, and the weight of the cobalt deposit noted.

The coulometer dish was emptied, carefully rinsed, dried and weighed, and the weight of silver deposited taken as a measure of the current passed. As previously mentioned, the number of equivalents of silver deposited was in good agreement with the number of equivalents of cobalt deposited on the cathode. The latter, however, was generally slightly lower.

Note: (After the current had been passed through the coulometer in the reverse direction to re-deposit the silver on the silver bar, the dish was cleaned with HNO_3 . On this addition, a brown color was produced. This was probably due to the presence of organic silver compounds from the filter paper. Rosa and Vinal⁽²⁴⁾ state that the error due to filter paper is 1-5 parts per 10,000. This is well within the limits of experimental error.)

Then, the two halves of the apparatus were separated and stoppered. The exterior of the glass was wiped off and the apparatus and contents weighed. The solution was well mixed, poured out into dry flasks and the tubes rinsed, dried and weighed.

The 5 portions were then analyzed electrolytically, and the transfer of electrolyte was calculated.

The anode results could not be relied on, as has been explained previously.

The amount of solution taken for analysis was such as would contain from 0.15 to .25 gms. of cobalt. Smaller

amounts would be less accurate and greater amounts were difficult to plate out with quantitative accuracy.

On account of the great dilution necessary to accurately measure this amount of cobalt, at high concentrations, some of these solutions were analyzed by determining their densities, and finding the corresponding concentration from the density concentration curve which is shown later.

TABLE IV

Transference Numbers of CoSO₄ Solutions

1	2	3	4	5	6	7
Concentration (Equiv/ Liter)	Time	Current (M.A.) (Approx)	Faradays Passed	Equiva- lents Lost by Cathode Solution	4 minus 5	Trans- fer- ence Number of Co
N=3.944	7-H	36	.006627	.005640	.000987	.149
3.104	4-H	25	.005624	.004320	.001304	.232
2.833	3-H 15 Min.	60	.010504	.007776	.002728	.260
2.331	4-H 30 Min.	19	.003335	.002408	.000927	.278
1.860	2-H 40 Min.	60	.008620	.006154	.002466	.286
1.454	4-H 30 Min.	18	.003176	.002195	.000981	.309
1.444	4-H	18	.002632	.001801	.000831	.316
1.066	6-H	20	.00443	.00325	.00118	.266*
0.996	4-H 30 Min.	46	.007536	.004850	.002686	.356
.753	4-H 15 Min.	15	.002550	.001854	.000696	.373
.473	4-H 30 Min.	20	.002929	.001787	.001142	.390
.233	4-H	16	.002610	.001577	.001033	.396

* Not plotted on curve

These results are the latter of a series of approximately 35 determinations. The earlier results were unreliable, mainly due to lack of standardization of apparatus.

No results were discarded unless an experimental error was detected.

Results and Calculations

Since the anode was of cobalt, the amount of cobalt dissolved from it by electrolysis would be equal to the amount deposited on the cathode, if no other reactions occurred. Therefore, the amount of CoSO_4 in the solution between the electrodes would be the same before and after electrolysis. Thus the amount of cobalt lost by transference in the cathode solution would be equal to the amount gained in the anode solution.

That there are anomalous anode phenomena has been discussed already. On this account the cathode results alone were used in the calculations.

From the amount of cobalt found by analysis in a measured volume of the original solution, the volume concentration was found. Then, by reference to the Density-Concentration curve, the weight concentration was found and the ratio, CoSO_4 to water, determined.

Similarly the ratio CoSO_4 to water was calculated for the cathode solution after electrolysis. From the total weight of the cathode solution, the total weight of CoSO_4 associated with the water, (considered as constant) both before and after electrolysis, was found. Then, by subtraction, the loss of CoSO_4 was found. This quantity represents the amount of cobalt deposited on the cathode, minus the amount which had migrated into the cathode compartment.

The number of equivalents of cobalt deposited could be found by weighing that electrode before and after electrolysis, or, more accurately, from the amount of silver deposited in the coulometer.

Therefore to find the number of equivalents of cobalt which had migrated into the cathode solution, we must subtract the number of equivalents which the cathode solution lost, from the number of equivalents of cobalt deposited on the cathode.

Then the transference number of cobalt is equal to:

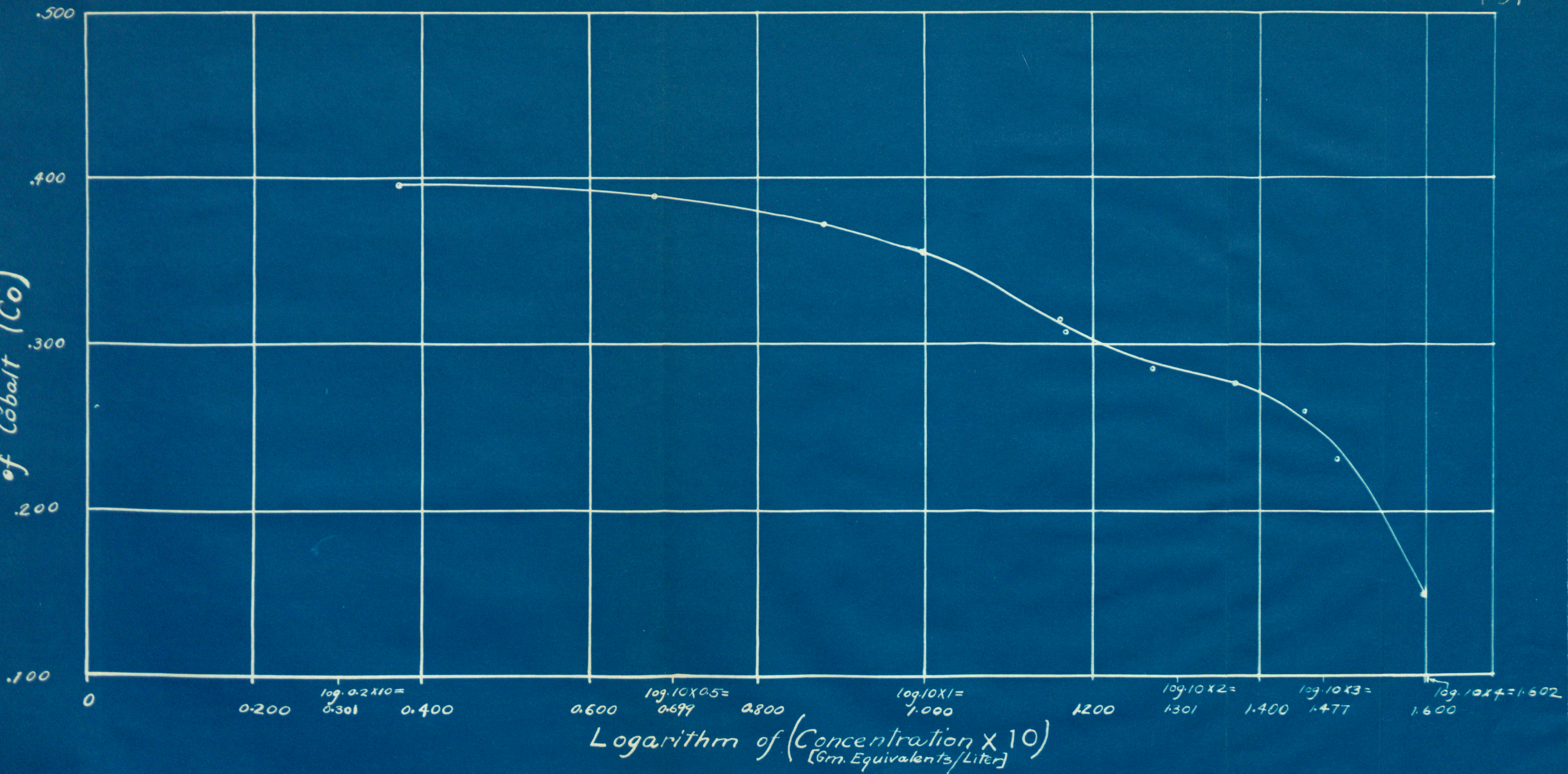
$$\frac{\text{Equivalents Co}^{\text{++}} \text{ moved into cathode solution}}{\text{Equivalents Co}^{\text{++}} \text{ deposited on cathode}} \quad \text{or}$$

$$T_{\text{Co}}^{\text{++}} = \frac{N - \text{Equiv. Co}^{\text{++}} \text{ lost to cathode solution}}{N}$$

N = No. of Faradays of electricity passed.

A similar calculation could be made with the anode results, if such were reliable.

It is obvious that the transference number would be negative if the loss in cobalt by the cathode solution were greater than the amount of cobalt deposited on the cathode.



TRANSFERENCE NUMBERS OF $CoSO_4$ SOLUTIONS
Figure VI

Discussion of Results

Berger⁽²⁾ found for the equivalent conductance of cobalt sulfate at infinite dilution the value $\Lambda_0 = 134.6$ mhos for 25°. The ion-conductance of $\overline{\text{SO}}_4$ at 25° is 78.4. Hence the ion-conductance of Co^{++} is found to be 56.2.

The transference number of Co^{++} in CoSO_4 is therefore $\frac{56.2}{134.6} = 0.419$ for solutions of zero concentration.

An examination of Table IV shows at once how greatly the determined transport numbers deviate from the value calculated for zero concentration. The measured values vary from 0.396 for a 0.233 normal solution to 0.149 for a 3.994 normal solution.

These results indicate that with increasing concentration either there is a very great change in the ratio of the mobilities of the cobalt and sulfate ions or that there is the appearance of complex anions in increasing concentration as the solutions increase in stoichiometrical concentrations.

If we consider that the rapid decrease in the transference numbers with the concentration is due to a change in the ratio of the ion mobilities, a possible explanation suggests itself in excessive hydration of cobalt ion. It is necessary to assume that each cation is much more highly hydrated than the sulfate ion. Suppose that

each Co^{++} ion carries ten molecules of bound water more than the anion. During transference this water is carried to the cathode, thereby displacing the whole solution towards the anode. Then for one Faraday carried by Co^{++} , there would be an apparent movement towards the anode of 5 moles or 90 grams of water. For the 0.233 N. CoSO_4 solution this would give $0.233 \times 0.09 = 0.021$ equivalents change in the apparent migration. But this is further reduced in proportion to the transport number of Co^{++} . If we use the value for $T_{\text{Co}^{++}}$ for zero concentration, this gives $0.021 \times 0.42 = 0.009$ for the total effect on the migration. The actual change in migration is $0.419 - 0.396 = 0.025$. This method of explanation is, therefore, inadequate to explain our results. A correction of two and one-half times greater would be required to explain them away. Even if we assume the value 0.396 for $T_{\text{Co}^{++}}$ at .233N, to be somewhat low in regard to the value, $T_{\text{Co}^{++}} = .419$, at zero concentration, and using its highest probable value (.410) we must still assume at least 10 molecules of water attached to the (Co^{++}) ion in excess of that attached to the ($\overline{\text{SO}}_4$) ion. At higher concentrations, the hydration would have to be greatly increased. Such great hydration seems very improbable.

The second explanation lies in the admission that we are dealing here with complex ions, such as $\text{Co}(\overline{\text{SO}}_4)_2$.

Pfanhauser (25) found that in a saturated solution of nickel ammonium sulfate, the nickel moves entirely to the anode in the form of the complex ion, $\text{Ni}(\overline{\text{SO}}_4)_2$. Thus there

is nothing revolutionary in postulating a similar phenomenon in the case of cobalt sulfate especially as the complex ion $\text{Ag}(\overline{\text{CN}})_2$ is readily admitted. The decreasing values of the transference numbers of Co^{++} are due to the increasing amounts of cobalt carried to the anode as complex $\text{Co}(\overline{\text{SO}}_4)_2$ ions.

It appears to be significant that the change in direction in the $T_c - \log C$ curve occurs at approximately the same concentration as the break in the Density-Concentration curve. At the present time no explanation is offered for these changes in direction. It is hoped that a mathematical analysis of the density results will throw some light upon the meaning of the "break".

SUMMARY AND CONCLUSIONS

The transference number of Co^{++} in cobalt sulfate solutions at concentrations 0.233 to 3.994 N. has been measured at 25°C.

In this range the T_C values vary from 0.396 to 0.149. The value calculated from the ion conductance is 0.419. It has been shown that the assumption of excessive hydration of the cobalt cations is inadequate to explain the deviations of the T_C values from 0.419.

It has been suggested that the admission of the presence of complex anions of the type $\text{Co}(\overline{\text{SO}}_4)_2$ affords a much more logical explanation.

The densities of cobalt sulfate solutions at concentrations .020 to 4.674 N. have been determined at 25°C.

It has been pointed out that the break in the Density-Concentration curve occurs approximately at the same concentration as the change in the direction of the T_C - log concentration curve. The explanation of this "break" is reserved for further investigation.

ACKNOWLEDGMENT

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