DETERMINATION OF THE STANDARD ELECTRODE POTENTIAL OF
COBALT

By

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INTRODUCTORY STATEMENT

The standard electrode potentials have been determined for most of the common, more abundant metals from electrodes possessing a high degree of constancy and reproducibility, and are conveniently tabulated in International Critical Tables.

Considerable study of the cobalt electrode has been reported, but results are not in agreement, and conditions were such that Gerke does not include any of these in the above mentioned tabulation.

Since cobalt is closely related to nickel and has possibilities for use instead of it in the electroplating and electroforming industries, the need for a precise determination of its electrode potential is evident.

REVIEW OF LITERATURE

The cobalt-cobaltous potential has been studied by Neumann (1), Labendzinski (2), Foerster and co-worker (3), Denham and Pennycuick (3a), but more especially by Schildbach (4), and Lamb and Larson (5). The electrode behavior has been studied by Smits (14) from the viewpoint of the theory of allotropy, and considerable work has been done in the fields of electrodeposition and overvoltages, but results from these latter are so variable as to have little meaning for the problem and will not be considered further.

It is Schildbach's value (loc. cit.) of -0.29 for the normal potential measured in cobalt chloride solution, using finely divided cobalt which is reported in most of the text books of the day.

Lamb and Larson (loc. cit.) for the sake of comparison calculated the previous values to 25° C and normal potential conditions, reporting them as follows:

Neumann. Co plated on Pt. in $CoCl_2$	-.262
Labendzinski. Co plated on Pt. in $CoCl_2$	-.307
Schildbach. Finely divided Co in $CoCl_2$	-.292
Lamb and Larson. Co. on Pt. using $CoCl_2$	-.255 ± .007

In addition to these the following should be noted:

Cofetti and Foerster. Co in $CoCl_2$ -.290

Denham and Pennycuick. Co on Pt in $CoCl_2$ -.204

Schildbach. Co powder in $CoSO_4$ -.312

Schildbach. Co on Pt. in $CoSO_4$ -.288

the two latter being in vacuo, in normal solutions, while the other measurement of Schildbach's was in nitrogen with the cobalt chloride solution one normal.

For practically all these measurements the reference electrode was the normal calomel cell,

$$Hg/Hg_2Cl_2, \; N \; KCl/ \; (=.2822),$$

so the cells contained a liquid junction potential of unknown value. In addition to this, concentrations of the solutions used, purity of materials, temperature control and technique in carrying through a determination, were so varied that too much weight cannot be attached to the failure of the above results to agree.

The above mentioned measurements were all made in solutions where the concentrations were expressed in terms of molar (or normal) values whereas standard potentials, by definition use molal concentrations.

Also, oxygen if present, tends to lower the potential of the metal, and this seems to have been the case in the measurements of Lamb and Larson.

Since cobalt is a very stiff metal the determination of its potential presents the greatest difficulty. Conditions of strain in the surface, when once established will persist almost indefinitely; the surface may be easily affected by

adsorbed or dissolved hydrogen; even the small amount of oxygen present in the usual cobalt salt solution produces a pronounced drop in potential, and by the same token exposure to air results in a similar error; finally the metal exhibits to a considerable degree the phenomena of passivity.

In view of all the above it would appear that cobalt plated on platinum is liable to have conditions of strain which may lead to erroneous results. Save for the one measurement by Schildbach this was the form of metal used throughout the previous work.

CONVENTIONS AND TERMS

1. Standard Potential of cobalt shall mean the potential of the metal when in contact with a solution of its ions at unit activity.

2. Normal Potential shall mean the electrode potential when the solution bathing the electrode contains one gram equivalent of the ion in question per liter.

3. Molal Solution shall mean a solution containing one mole of the solute per 1000 grams of solvent.

4. ΔH, ΔF, ΔS, ΔCp, according to the nomenclature of Lewis (6) shall signify the heat of reaction, change in free energy, change in entropy and change in heat capacity, respectively.

5. The sign of the electrode shall be that of its charge when in contact with a solution of its ions. Accordingly we write for cobalt (-). This is the convention adopted by The American Electrochemical Society, the United States Bureau of Standards, the Bunsen Gesellschaft, the International Union of Pure and Applied Chemistry, and International Critical Tables.

The literature reports no values for the activity coefficients of cobaltous sulfate, but it has been shown that salts of the type $MeSO_4$ tend to behave as a group and the values given for these by Lewis and Randall (6) may be used. Hampton (7) found he obtained reproducible potentials when he assumed this for ferrous chloride in relation to barium chloride, and Haring and VandenBosche(8) likewise for nickelous sulfate in a case similar to the one under consideration.

MATERIALS

Water. This was prepared by taking the middle
third of the distillate when distilled water was re-
distilled in an all Pyrex glass apparatus using
permanganate in the residual liquid. Since the solutions
were to be boiled before use no attempt was made to exclude
carbon dioxide.

Cobalt sulfate. Since all of the "Chemically Pure"
cobaltous sulfate contains some nickel as sulfate, the
following method was used in an attempt to remove this.
Potassium cobaltinitrite was prepared following the method
of Biltz, Hall and Blanchard (9), except a motor driven
stirrer was used. This was washed five times with an alcohol
water mixture and recrystallized twice. This was decomposed
with the calculated amount of sulfuric acid, the acidity
adjusted by addition of ammonium hydroxide, and the cobalt
precipitated as the sulfide following the method of Haring
and Leatherman (10). The sulfide was filtered with suction,
the precipitate again placed in water, and stirred vigorously
in order to free from absorbed impurities. This washing and
filtering was repeated six times. The sulfide was then treated
with hot, concentrated sulfuric acid until in solution. The
solution was diluted, filtered, evaporated to dryness to expell
excess sulfuric acid, taken up in water, again filtered, and

recrystallized three times. The presence of nickel, iron and alkali metals could not be detected in this product.

Iron was tested for as follows: 2 grams of the sulfate were dissolved in 20 cc of water, a few drops of nitric acid added and the solution boiled. Ammonium hydroxide was added until the precipitate first formed dissolved. This was filtered, the precipitate, if any, washed with water, and dissolved in hydrochloric acid. Treatment with potassium thiocyanate failed to give any color. This should show the presence of .03% of iron.

For the alkali metals the test was carried out by precipitating 4 gm. of the cobalt as sulfide with addition of a little ammonium hydroxide to counteract the acid liberated. The solution filtered, the filtrate evaporated, the last part being evaporated in a crucible, then ignited and weighed. There was no appreciable residue. This should detect .1%.

For nickel 1 gram of the salt was dissolved in 20 cc of water, 1.5 grams of sodium cyanide added and the solution warmed until it was yellowish, when it was filtered. The filtrate was cooled, 1 cc of bromine added, shaken until the bromine dissolved and 10 cc of 15% sodium hydroxide added. No precipitate resulted. This was repeated with double the quantities of reagents in the same volume of water. No precipitate resulted. This is capable of detecting .01%

nickel.

These tests were based on those given in "Murray" (11a).

Plating Solution. This was similar to that recommended for the electroplating industry. It was 1 N in cobaltous sulfate, .25 N in ammonium chloride and .25 M in boric acid.

Cobalt. The metallic cobalt was prepared by electrolyzing some of the above plating solution between platinum electrodes (anode = Pt foil, cathode = 1 cm. of #24 guage Pt wire) in a solution maintained at about 75-85°C using a current density of about 16 amps/sq. cm. This gave a deposit of finely divided metal which could be removed from the cathode from time to time by touching with a glass stirring rod. The metal so prepared was washed with some of the solution to be used and was kept under the liquid thereafter. The solution was always hot, freshly boiled for the washing. The metal was used as soon as prepared.

Mercury. The method of Hulett and Minchin (11) was followed for the purification of this material. Ordinary good grade mercury was passed through a long column of 1 N nitric acid and mercurous nitrate in the form of a fine spray for four washings. It was then distilled twice in a current of air under reduced pressure in an apparatus made in one piece of Pyrex glassware.

Mercurous sulfate. This salt was prepared according to the method of Hulett (12). 1 N sulfuric acid was electrolyzed at a current density of 0.9 amps/dem., using a platinum foil cathode and a pure mercury anode. The mercury surface was swept clean by a slowly rotating glass arm. The product so prepared was kept under 1 N sulfuric acid in a glass stoppered bottle away from the light. Before use it was washed as directed by Wolff and Waters (13).

APPARATUS

The cells were maintained at constant temperature in an air thermostat regulated at 25° C $\pm$ .15°, and were kept under these conditions for 24 hours before final measurements were taken. The thermostat was constructed with a wooden frame, covered with 3/4 inch plank over which was a layer of "Prestwood", while the inside was lagged with 1/4 inch asbestos. There was a 1 inch air space between the planking and the asbestos. Mixing of the air was assured by means of a high speed fan. A mercury regulator with an Aminco supersensitive relay controlled the temperature.

Measurements were taken with a Leeds and Northrup Type K Potentiometer, using a Type R Galvanometer. An Eppley standard cell was used. All volumetric apparatus and weights were carefully calibrated. The thermometer was calibrated against one calibrated by the Bureau of Standards. The pychnometer was calibrated using freshly boiled distilled water. All density measurements were taken using a water thermostat controlled to 25° $\pm$ .02°.

Similar electrode vessels were used for both the reference and cobalt electrodes, except the latter were modified as described under "Procedure". They were of the type recommended by Smits (14) but modified as described

and successfully used by Haring and VandenBosche(loc.cit.)
but slightly changed as described later.

PROCEDURE

Some of the warm plating solution was introduced
into the electrode vessel and the cobalt deposited on the
sealed-in platinum cathode at high current density. The
solution was then decanted and the electrode washed four
times with hot, freshly boiled portions of the solution to
be used. Then with some of the latter solution in the
vessel, freshly prepared cobalt metal was introduced, care
being taken that it was kept moist as this was carried out.
The electrode was then connected to the filling vessel and
pumped out for some time to rid of absorbed hydrogen, as
it was found that this persisted tenaciously, and then filled
by breaking the suction. At first rubber stoppers were
used for sealing the vessel. These were sealed with
DeKhotinsky cement, but the seals were found to be unsatis-
factory, so for the final measurements the top of the vessel
was sealed off. This introduces the danger of adsorption
of fuel gases by the solution during the sealing process, but
since pumping and boiling out followed immediately it was

assumed that these were removed if such was the case.

Other manipulative details were essentially those given in the report of similar work by Haring and Vanden-Bosche (loc. cit.).

Since boiling affects the concentration of the cobalt sulfate solutions, it was necessary to determine the concentration after a measurement. Also since dilute cobalt solutions of the dilution and quantity used here are a bit difficult to obtain reliable results with by the usual electrolytic or other quantitative methods it was decided to plot densities against molalities and use this curve for the analysis of the solution afterward, determining the densities of the solutions from the cells and reading off the corresponding molalities. Values in the literature do not cover the concentration range desired or else were lacking in concordancy, so a number of solutions were made up carefully, the densities taken, and analyzed electrolytically. It was found that the water content of the crystals was not constant enough to weigh up the salt for a solution of a given molality directly, if the analysis is to be taken as a criterion, since the latter were slightly lower for a given determination. Completion of electrolysis was determined by testing with nitroso-beta-naphthol as directed by Yoe (15).

The method of electrolysis was a modification of
that given in the literature. It had been worked out by
Mr. F. H. Evans (16) in this laboratory, and found to give
results that were checking at about .02% low.

For an analysis from .2 to .25 of the metal as the
salt was taken. To this was added 3.3 grams of boric acid,
7 grams of ammonium sulfate, and 25 cc. of concentrated
ammonium hydroxide (sp. gr. = .9). The solution was
diluted to 100 cc., heated to 90°C, and electrolyzed
without further heating at 1 ampere and 3.5 volts using a
gauze cathode (Winklerform) and a rotating anode of
platinum. From 1.5 to 2 hours were needed for the completion
of electrolysis. When this was complete as shown by test,
the solution was pipetted off, keeping contact, and running
in water during the process. The pipetting was carried out
four times, after which the electrode was removed with the
current on and washed with water and alcohol before drying
high above a flame for weighing. Densities for a given
concentration could be checked to $\pm$ .00003 but difficulty
was experienced in checking molalities to closer than
$\pm$ .0002, so that while density date for the cells would
indicate greater accuracy than this it should be borne in
mind that the curve from which the corresponding molalities
are read is less accurate. Actually, the effect on the
E. M. F. for a cell is inappreciable.

The densities and molalities obtained by this method are given in Table I. Since a few measurements were made on cobalt chloride solutions, density and molality data for this salt were taken from the literature (18) and the data obtained by extrapolation of the curve for this are given in Table II.

Activity data for cobalt sulfate and cobalt chloride over the desired concentrations are not known, but were obtained as mentioned elsewhere. There is some data available (6) which indicates that the activity for cobalt chloride should be slightly greater than that for the barium halide, but this is probably not a serious discrepancy.

There is one rather interesting by-product of the density-molality results. This is with respect to the partial molal quantities. If we plot the volume of solution containing 1000 grams of water against the molality, the tangent to the curve will give the partial molal volume of the solute. This plot gives at .01 molal $\bar{v}2 = -7.25$ at .05 about -3.2 and an increase to zero at about .13 M, with a positive value after this; at .15 M becoming about 4.5. In words, for the dilute solution the addition of more solute actually diminishes the total volume of the solution.

Table I

Densities of Cobalt Sulfate Solutions at
25°C, Referred to Water at 4°C.

Molality	Density
0.04	1.00330
0.05	1.00481
0.06	1.00642
0.07	1.00795
0.08	1.00951
0.09	1.01108
0.10	1.00261
0.11	1.01409
0.13	1.01732
0.15	1.02041

Table II

Densities of Cobalt Chloride Solutions at
25°C Referred to Water at 4° C.

0.04	1.00165
0.05	1.00276
0.08	1.00623
0.10	1.00854
0.15	1.01430

Table III

Data for the Calculation of Normal Potentials*

Normality	Density*	N/
.5	1.0380	.26327
.2	1.0158	.32608
.1	1.0079	.37978
.05	1.0040	.44262
.01	1.0020	.53797
.005	1.0009	.61499

*Note 1. Taken from J. A. C. S. 52, 2653 (1930) Cantelo and Berger. Conductance of Cobalt Sulfate Solutions.

*Note 2. Densities are at 25° referred to water at 25°. The data at lower concentrations is slightly non-concordant.

DATA AND RESULTS

I. Preliminary Work.

Considerable work was carried out using half cells closed by a rubber stopper and sealed with De Khotinsky cement. The cells were eventually found to be incompletely sealed. The first group were of 0.15 M concentration. The reference cells were found to check within $\pm$ .00003 volts. Cell #2 may be cited as typical under these conditions.

Voltage	Time
.97659	6 hrs.
.97244	24 "
.96962	48 "
.96860	72 "
.96780	96 "
.96650	120 "
.96395	168 "

They showed a tendency to become constant at a value which gave for the standard potential about .237. It was practically always noted that the metal had become brownish, or in some cases had a blue tint. Data are given below for three typical cells of this series. #12 for example, was carried along for

24 days, the last seven of which it was constant. In the previous 17 it had dropped 8 millivolts.

Table IV

Cell #	Density	Molality	γ	Eobs	Eo
6	1.01852	.1384	.135	.960	-.238
7	1.01855	.1385	.135	.961	-.238
12	1.02879	.2045	.101	.973	-.237

As previously mentioned the method of sealing was eventually abandoned, and further work carried on under the new conditions.

FINAL MEASUREMENTS

It would appear that the slow drop in potential
with time noted previously must be due to the infiltration
of oxygen when the electrode vessel is raised from the
mercury seal into the oxygen (air) saturated solution
above it, for even with the new technique of sealing there
was still a slow drop in the observed value. Since the
solutions were warmed on filling, the initial readings,
if taken within a few hours after placing in the thermostat,
were always low. Within twenty-four hours they reached
thermal equilibrium, and the potential dropped very slowly.
The more often the electrodes were raised from the seal for
measurement, the greater was the drop per day. These facts
are brought out by a comparison of cells 19 and 61 shown
below. Cell 61 was measured at 8, 24, and 48 hours, and then
kept sealed for 8 days.

Table V

Cell #19	Days	Cell #61
1.00061	8 hrs.	1.00875
1.00218	24 hrs.	1.01255
1.00190	2	1.01260
1.00173	3	
1.00108	4	
1.00080	5	
1.00054	6	
1.00048	7	
0.99996 ·	8	1.01156
0.99923	11	
0.99441	14	

For the greater number of the measurements the cells were placed in the thermostat for 24 hours, and the measurement taken at the end of this time. They were then analyzed for molality by determination of the density.

Five different concentrations were run, using reference electrodes at .05, .075, .10, .125 and .15 M. For the .05, .10 and .15 concentrations six reference cells were set up at the same time, and were found to check well at all times. For the other two concentrations two cells each were set up and were also found to check well.

Two were also set up at .03 M, but results were low for
this concentration. It seems probable that the solubility
of mercurous sulfate begins to be appreciable at this molality.

Cells were polarized anodically and cathodically and
were found to return to the equilibrium value. However,
too much weight cannot be attached to this, since cells which
failed to give the accepted value also behaved similarly on
polarization.

Since the cells are boiled out on filling there is a
slight change in concentration, so that in most cases the
final cell contained a slight concentration potential, which
in extreme cases might amount to as much as a millivolt, and
was corrected for.

A summary of the results are given in Table VI.

Table VI

Part A.   Reference = .15 M.

Cell #	Eobs.	Density	Molality	γ	Eo
19	1.001	1.02237	.1621	.121	.279
20	1.004	1.02195	.1595	.126	.282
21	0.9997	1.03048	.2120	.108	.281
59	1.001	1.01890	.1408	.134	.278
62	0.999	1.02198	.1596	.126	.277
73	0.999	1.02193	.1591	.127	.277

Part B.   Reference = .125 M.

Cell #	Eobs.	Density	Molality	γ	Eo
66	1.001	1.01680	.133	.137	.278
67	1.001	1.01715	.129	.140	.276

Part C.   Reference = .10 M.

Cell #	Eobs.	Density	Molality	γ	Eo
47	1.002	1.01442	.1118	.150	.276
48	1.002	1.01469	.1133	.149	.276
50	1.005	1.01177	.0942	.160	.276
51	1.011	1.01559	.1213	.145	.286
53	1.004	1.01693	.1276	.140	.279
55	1.002	1.01443	.1118	.150	.276
56	1.003	1.01469	.1132	.149	.276
57	1.004	1.01470	.1133	.149	.278
58	1.003	1.01442	.1124	.150	.277
60	1.003	1.01462	..1120	.150	.276
63	1.003	1.01530	.1175	.146	.277

Table VI (Cont'd.)
Part D, Reference = .075 M.

Cell #	Eobs.	Density	Molality	Υ	Eo
64	1.007	1.00991	.0825	.170	.276
65	1.008	1.00933	.0790	.174	.277
69	1.008	1.00920	.0780	.175	.277

Part E. Reference = .050 M.

44	1.016	1.00466	.0492	.222	.278
38	1.014	1.00584	.0577	.206	.279
39	1.015	1.00450	.0480	.223	.277
40	1.015	1.00446	.0479	.223	.277
42	1.016	1.00466	.0492	.222	.279
43	1.017	1.00473	.0495	.220	.279
44	1.016	1.00466	.0492	.222	.278
61	1.013	1.00530	.0530	.2135	.276

Part F. Reference = .03 M

| 45 | 1.017 | 1.00200 | .0325 | .265 | .275 |
| 46 | 1.015 | 1.00261 | .0361 | .253 | .273 |

Rejecting the values for Cells #20, 21 and 51 as well as
those at .03 molal as these are not consistent with the
others, for reasons noted elsewhere, we get an average
value = -.2777 or -.278 $\pm$ .002

FURTHER STUDIES

A. Amalgam electrodes. An attempt was made to prepare an amalgam electrode, but it was found unsatisfactory from the standpoint of boiling out, filling and sealing so was not used. One set up at .1 M without boiling gave E obs. = .986.

B. An attempt to ascertain the effect of free acid or hydrogen ion on the potential was made by adding a small quantity of sulfuric acid to one cell at .1 M. Hydrogen was liberated equal to about a cc of the gas and the potential was .980.

C. It was noted in Cells 20 and 21 that the plated portion of the electrode may have been exposed. It was thought that this might make the potential slightly higher. Accordingly two cells were set up using the platinum wire plated with cobalt only, with the finely divided metal absent. Only one boiling out was needed, so there was practically no concentration change. The values for the two cells did not agree.

				γ	
1	1.034	1.01260	.10	.158	-.308
2	1.023	1.01260	.10	.158	-.296

This would indicate that the metal in this condition is strained or else, in spite of all precautions the finely

divided metal of the research is affected in some manner so that it gives a lower potential. It should be pointed out that if we take the measurements of Schildbach or Labendzinski in a solution .05 molar, and assume it to be molal and calculate Eo values using a correction factor found from some work to be discussed later, we get values which are in fair agreement with the above. Thus from Labendzinski's cell (loc. cit.)

$$Co/CoCl_2 \ .05 \ Molar \ KCl \ N/ \ Hg_2Cl_2/ \ Hg = .625$$

$$Eo = -.305$$

And from the similar cell from Schildbach (loc. cit.)

$$Co/ \ CoCl_2 \ .05 \ Molar/ \ KCl \ sat./KCl \ N/Hg_2Cl_2 \ / \ Hg = .622$$

there is obtained Eo = -.303.

STUDIES USING COBALT CHLORIDE

It was thought that the presence of oxygen in the cells used by Lamb and Larson (loc. cit.) may have caused the comparatively low results they report. Hence an attempt was made to check their values. Two cells were set up at .05 molal (not boiled out) and measured against mercurous chloride reference electrodes. Two of the latter and two of the cobalt cells, were set up at the same time. In addition to the two normal calomel cells two calomel cells with/liquid junctions were set up for comparison. The value of the normal calomel cell is +.2822 and of the calomel + .2700 as reference electrodes. The platinum electrodes were plated using the regular plating solution. The cobalt chloride was ordinary good grade "chemically pure" material containing as chief impurity 0.1% of nickel as chloride. The mercurous chloride was high quality material which had been used in experimental work in the laboratory with consistent results.

One cell was set up using an electrode plated from a cobalt chloride solution since this was one of the ways used by the previously mentioned authors. The coating was non-adherent due to the high current density used, but this is shown in the tabulation below also.

Finally, two cells were set up using finely divided

material as with the cobalt sulfate cells. And the
results for these are also recorded in the following
tabulation. It will be noted that these two measurements
check the average of the previously found sulfate values
very well.

Table VII

Cobalt Chloride Cells Prepared in a Manner Similar
to that of Lamb and Larson

Cell #1   With Calomel as reference.

$$Co/ \; CoCl_2 \; (.05M)/\underset{N}{Hg_2}\underset{KCl}{Cl_2}/Hg = .556$$

Cell #2   As above   = .557

Cell #1   Without liquid junction potential.

$$Co/CoCl_2 \; (.05)/ \; Hg_2Cl_2/Hg = .615$$
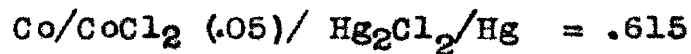
Cell #2   As above   = .616

The difference between the two is .059 volts, whereas the
difference between the reference electrodes is .013 in the
opposite direction.

These measurements with normal calomel or reference give
for the normal potential of cobalt a value = -.255, which
is in excellent agreement with that of the previously
mentioned authors. Also if we calculate the standard
potential the value .233 is obtained in good agreement with
the previously mentioned work of the present research when

oxygen leaked into the cells.

The one electrode plated from cobalt chloride
was as follows:

$$Co/\ CoCl_2\ (.05\ M)/Hg_2Cl_2/Hg\ =\ .576$$
$$N\ KCl$$
$$Co/\ CoCl_2\ (\ .05M)Hg_2Cl_2/\ Hg\ =\ .635$$
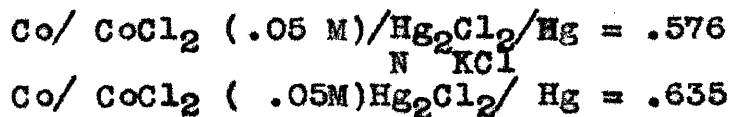
Table VIII

Cobalt Chloride Cells Prepared in a Manner Analogous
to the Sulfate Cells.

Cell #	Eobs	Density	Molality	γ	Eo
1	.658	1.00475	.0670	.545	-.278
2	.657	1.00477	.0673	.545	-.277

Using the normal calomel cell as reference for #1 gave a
value = .598 volts, where the difference = .060

The equation from which these are calculated is:

$$Eobs.\ =\ Eo\ -\ .08873\ \log \sqrt[3]{4}\ \gamma m$$

based on the reaction

$$Co\ +\ Hg_2Cl_2\ =\ Co^{++}\ +\ 2Cl^-\ +\ 2Hg$$
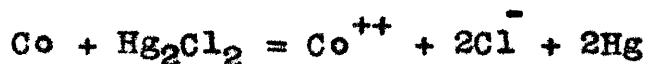
One cell was set up similar to the above and an attempt
made to take temperature coefficients. Due to the fact
that ice had to be used in the thermostat (air) this was
not so very satisfactory.

Cell #	Eobs.	Molality		Eo	
3	.659	.0597	.553	-.276	

Temp.	dE/dT	Eobs.	ΔH	ΔF	ΔS
25	.0002	.65882	33,148	30,404	9.22
28	.0002	.65821			

As a check on the reliability of this we may calculate
the heat of formation of cobalt chloride using this data
and compare it with that from calorimetrically determined
values. This calculation is carried out on page 44 as
well as a similar one for the sulfate.

UTILIZATION OF THERMODYNAMIC DATA FOR THE CALCULATIONS
OF ELECTRODE POTENTIALS

Using known values of a number of atomic entropies, Sackur (18) showed that the constant in the thermodynamic equation for the entropy of an ideal monatomic gas, could be separated into two terms, one a function of the atomic weight of the gas, and the other a constant independent of the nature of the gas. Thus the equation

$$s = 3/2R \ln T + R \ln v + \text{constant}$$

may be written as

$$s = R \ln (T^{3/2} w^{3/2} v) + C = R \ln (C' \, T^{3/2} w^{3/2} v)$$

where C' and C $(= R \ln C')$ are universal constants. His attempt to evaluate these constants from the quantum theory failed to check experimental work. Tetrode (19) made a calculation which more nearly checked found values.

Lewis and Adams (20) showed that the dimensions of every physical quantity could be reduced to a power of a single dimension, which they took as a length. This makes it possible to express every quantity in terms of a single unit in this way reducing seconds, grams, ergs and degrees to centimeters, calling these Ultimate Rational Units, (U. R. U.). Applying these ideas to the Sackur equation we get

$$s = R \ln (T^{3/2} w^{3/2} v) - 11.39$$

or

$$s = R \ln (T^{3/2} w^{3/2} v \times 3.252 \times 10^{-10})$$

which at 25 degrees and 1 atmosphere, substituting for
v from the gas law, gives

$$S = 3/2R \ln w + 25.70$$

Latimer and Buffington (21) showed that for divalent
ions such as beryllium and strontium the entropy of the
aqueous ion could be calculated using the equation

$$S_{aq.ion} - S \text{ gasion} = -9.5 + 94.5 (1/r)$$

where Sgas ion is the value from the Sackur equation
already given, for a monatomic gas at $298°K$ and one
atmosphere and r is the ionic radium. This was based on
the original Bragg radius for sodium, and the constants
should be slightly changed, but the validity of the
relation remains. Taking the entropy of hydrogen as
29.4 and of metallic cobalt as 7.2 from the calculations
of Lewis and co-workers utilizing the Sackur equation,
the principle of Ultimate Rational units and thermal data,
particularly heat capacities, we may proceed to the
calculation of change in entropy for the reaction

$$Co + 2H^{++} = Co^{++} + H_2$$
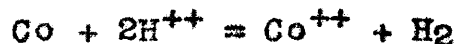
and having this apply the relation that

$$\Delta F = \Delta H - T \Delta S$$

and remembering that $\Delta F = -nFE$ we have at once the
potential of the cobalt electrode as accurately as the
various calorimetric data will allow it. The value for
the heat of formation of the aqueous cobalt ion taken

from International Critical Tables (Vol. V) is based on calorimetric data. It is probably in error to some extent, but may be used for purposes of illustration, and should give the potential to within a few centivolts.

The reliability of the electrode potentials calculated by this method is largely dependent on the accuracy of the heat of reaction. An error of one entropy unit affects the potential by .006 volts. It is difficult to estimate the accuracy of the heats of solution since heats of formation of the cobalt ion using different salts are not concordant. Moreover, the equations used give a value too high for iron, when its standard potential is calculated by the method; hence, since iron is rather closely related to cobalt it is practically certain that this calculated value for the latter is too high also.

CALCULATIONS OF THE ELECTRODE POTENTIAL

For the gaseous ion: (Ion of cobalt at 288.1° K)

$S = 3/2$ R ln at. wt. + 25.7

$\quad = 3/2$ x 1.9885 x 2.303 log 58.94 + 25.7

$\quad = 12.16 + 25.7 = 37.86$ cals / degree

For the aqueous cobalt ion:

$S = -9.5 - $ Sgas ion + 94.5 $(1/r)$

$\quad = -9.5 - 37.86 + 94.5$ $(1/r$ 1.38)

$\quad = -9.5 - 37.86 + 68.5 = 21.14$

or utilizing the graph given by Latimer and Buffington

$S = 23.14$ cals, and this will be used.

For the replacement of the hydrogen ion by cobalt ion

$$Co + 2H^+ = Co^{++} + H_2$$

$7.2 + 0 = -23.14 + 29.44$

$\quad \Delta S = -0.9$ cals per degree
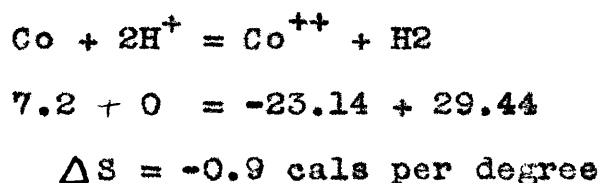
Solving for change in free energy:

$$\Delta F = \Delta H - T \Delta S$$

$\quad = -14,810 - (-.9 \times 298) = 14,542$ cals per gm. ion.

Solving for the standard potential in hypothetical one

molal solution:

$$\Delta F = -nFE \text{ or } -E = \Delta F / nF$$

$-E = 14,542 / \dfrac{2 \times 96,496}{4.185}$

$\quad = -.316$ volts at 25° C and one atmosphere pressure.

SUMMARY OF DATA UTILIZED IN CALCULATION OF THE
ELECTRODE POTENTIAL OF COBALT

Entropy of cobalt metal = 7.2 cals

Entropy of hydrogen = 29.4 cals

Radius of cobalt ion = 1.38 A$^{\circ}$

Heat of formation of $CoSO_4$ = 942,000 kj.

Heat of formation of H_2SO_4 = 880,000 kj.

Heat of formation of Co ion = 14,810 cals.

Entropy of cobalt gas ion = 37.86 cals.

Entropy of the aqueous ion = 23.14 cals

Change in entropy for the replacement of hydrogen ion by cobalt ion = -0.9 cals

Entropy change temperature product at 298.1 K = 268.2 cals

Change in free energy for the formation of cobalt ion = 14,542 cals.

The data for the entropy of cobalt metal and hydrogen are taken from Lewis and Randall, Thermodynamics Pg. 465. The radius of the ion from the radius of combination data of Bragg and Bragg "X-rays and Crystal Structure" Pg. 170 while heat of formation of cobalt sulfate and sulfuric acid are from I. C. T. V. Pgs. 191 and 178 respectively.

DETERMINATION OF THE TEMPERATURE COEFFICIENT OF
THE REACTION AND CALCULATION OF HEATS OF REACTION

For the reaction occurring in the usual galvanic cell, we may set up a calorimeter and measure the heat evolved directly or we may measure the electromotive force and its temperature coefficient and by use of the fundamental Gibbs-Helmholtz equation calculate the heat of the reaction occurring in the cell.

Since electrometric measurements are so much more readily carried out, and more precisely so at the same time, the values obtained are more reliable than those from calorimetric data.

In some cells it is possible to obtain more work than corresponds to the heat of reaction, because the cell cools off on operating and hence, according to the famous principle of LeChatelier is able to absorb heat from the surroundings and convert it in to useful work.

In other cells the maximum work is less than the heat of reaction, because the cell heats up on operating, and this heat coming from the cell is given to the surround-ings and is lost as useful work.

The usual expression for the Gibbs-Helmholtz equation is

$$E = \frac{-\Delta H}{nF} + T \frac{dE}{dT}$$

When the temperature coefficient is positive the electro-
motive force of the cell increases with rise in temperature,
such as is the case with the combination H_2/HCl (0.1M)/
Hg_2Cl_2/Hg while if it is negative, such as was found to be
the case in the cells under study here, the voltage drops
with increasing temperature.

In order to take measurements on the cells they
were held in the thermostat at 20, 25, and 30 degrees for
a minimum of 24 hours at each temperature, and were then
measured as usual. The results are not at all satisfactory
as the cells fail to be sufficiently reproducible to warrant
any great reliance in the results. It is highly probable
that the slow dropping of potential mentioned elsewhere
makes the slope of the temperature EMF. curve much less
steep than it should be, consequently making the heats of
reaction in error by as much as two or three percent or
more.

Having obtained the temperature coefficients at
two or three temperatures, and calculated the heats
corresponding, we may plot the latter against the temp-
erature and the tangent to this curve gives the change in
heat capacity for the cell reaction. In this way the
values for $\triangle Cp$ in Table XI were obtained.

Likewise if we know the specific heats of the

cobalt, mercury and mercurous sulfate we may calculate
the partial molal heat capacity of the cobalt sulfate
in the given concentration, and these are calculated for
the one cell. As mentioned previously much weight cannot
be attached to the values dependent on the temperature
coefficient measurements, because of the lack of complete
reproducibility of the electrodes.

Some further measurements were taken at different
temperatures on cells placed in a paraffin oil bath. Due
to the arrangement of the electrodes all of their surface
could not be immersed in the bath, the side arms being
outside. Difficulty was experienced in holding temperatures
constant long enough to attain equilibrium. It seems
probable that these measurements give temperature coefficients
which are low, so the truth may lie between the two.

From these measurements we may calculate not only
the heat of reaction, but also the change in entropy as
previously pointed out. If the desired accuracy for the
change in entropy is 0.1 cals per degree, which corresponds
to an accuracy of thirty calories in the change of heat
content, the temperature coefficient of electromotive force
must be accurate to .000004 volts per degree. For a ten
degree interval the electromotive force of a cell must be
reproducible to .00004 volts, although it is not necessary
for the cells to agree with each other better than .0001

volts. From this it can be seen that little weight
can be given these particular measurements for a cell
containing a stiff, easily disturbed metal like cobalt.

There is one point that might be mentioned
which indicates that the lower temperature coefficient
measurements are more reliable than the others. If we
take calorimetric data on the similar sulfate of iron
and from this calculate the partial molal heat capacity
for cobalt sulfate assuming it is similar to this, we
get a value which is fairly close to that obtained from
these measurements of electromotive force, whereas the
higher values give a quantity which deviates widely, not
only in magnitude, but in sign.

The table given below represents the data for
ferrous sulfate as recorded in International Critical
Tables Vol. V, Pg. 123.

If we plot percentages against specific heat
of the solution, the tangent to this curve at any concentra-
tion on extrapolation will give at its intercepts on the
100% water and 100% sulfate ordinates, the fraction by
which to multiply the molecular weight in each case to get
the partial molal heat capacities. At about 0.1 M this
gives for water $\bar{c}p \nleq 17.9$ and cobalt sulfate $=-18$ cals
per degree per mole.

Table VIII

Specific heat of Ferrous Sulfate solutions

at $25-45^{\circ}C$

Concentrations in percent	Specific heat in joules
1.0	4.093
2.0	4.000
5.0	3.892
10.0	3.633
15.0	3.474
20.0	3.335
25.0	3.200
30.0	3.066

Table IX

Results from Temperature Coefficient Measurements

Cell #41   M = .0443

Temperature	E.M.F. obs.	dE/dT
20	1.01200	-.000265
25	1.01095	-.000252
30	1.00986	-.000221

Cell #42   M = .0492

20.0	1.01637	-.000305
22.5	1.01576	-.000314
25.0	1.01555	-.000316
27.2	1.01450	-.000314
30.0	1.01388	-.000308

Cell #63   M = .1175

20.0	1.00420	-.000416
22.5	1.00340	-.000400
25.0	1.00263	-.000391
27.5	1.00188	-.000380
30.0	1.00118	-.000371

Table X

Calculation of Heats of Reaction, change in Free
Energy and Heat Capacities.

Cell #63   M = 0.1175

Temperature	$\triangle H$	$\triangle F$	$\triangle Cp$
20.0	-51,929	-46,300	65
22.5	-51,799	-46,275	62.5
25.0	-51,610	-46,238	62.5
27.5	-51,467	-46,203	52,5
30.0	-51,356	-46,167	39.6

Cell #41   M = 0.0443

Temperature	$\triangle H$	$\triangle F$
20.0	-50,213	-46,670
25.0	-50,083	-46,620
30.0	-49,670	-46,570

Cell #42   M = 0.0492

20.0	-50,990	-46,870
22.5	-51,122	-46,842
25.0	-51,175	-46,870
27.5	-51,136	-46,786
30.0	-51,067	-46,757

Cells in Paraffin Oil Bath for Temperature Coefficients

Cell #64   M = .0825

E. M. F.	Temperature	dE/dT
1.00761	20.0	-.00012
1.00732	22.5	-.00011
1.00714	25.0	-.00011
1.00680	27.5	-.00011

Cell #71   M = .0510

1.01412	20.0	-.00011
1.01390	22.5	-.00011
1.01364	25.0	-.00011
1.01360	27.5	-.00011
1.01338	30.0	-.00011

Cell #73   M = .1518

.99942	20.0	-.00011
.99928	22.5	-.00011
.99900	25.0	-.00011
.99885	27.5	-.00012
.99700	30.0	-.00014

For each of the above cells at 25°C

Cell #	ΔH	ΔF	ΔS	ΔCp	$\bar{c}p$
71	$^-$48,290	-46,776	-5.09	5	$^-$16
64	$^-$47,999	-46,477	-5.10	5	$^-$16
73	-47,616	-46,102	-5.04	5	$^-$16

Table XI

Tabulation of Results for Typical Cell

Cell No. 64

Temp.	ΔH	ΔF	ΔS	dF/dT	ΔCp	$\bar{Cp}$
20.0	-48,147	-46,501	-5.51	-5.51	8.0	-13
22.5	-48,009	-46,484	-5.12	-5.10	6.0	-15
25.0	-47,999	-46,477	-5.10	-5.10	5.1	-15.9
27.5	-47,972	-46,461	-5.08	-5.20	4.8	-16.2
30.0	-47,940	-46,465	-4.95	-5.70	4.0	-17.1

(See also work under "Studies on Cobalt Chloride")

CALCULATION OF HEATS OF FORMATION OF COBALT
CHLORIDE AND SULFATE

Nernst (17a) and Varet (17b) independently determined

the heat of formation of Hg_2Cl_2 as 62,600 calories

$$2Hg + Cl_2 = Hg_2Cl_2 \quad : \Delta H = 62,600 \text{ cals.}$$

$$Co + Hg_2Cl_2 = CoCl_2 + 2Hg \quad \Delta H = 33,148 \text{ cals.}$$

$$Co + Cl_2 = CoCl_2 \quad : \Delta H = 95,748 \text{ cals.}$$

$$\text{I. C. T. } \underline{V} \text{ value} \quad = 95,390 \text{ cals.}$$
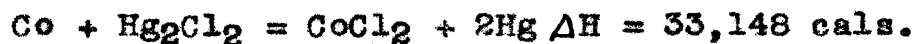
from the work of Biltz (17c) and Thomsen (24)

For the sulfate ---

Heat of formation is from Thomsen for the Mercurous

Sulfate, and from I. C. T. for cobalt sulfate and this

value is also based on Thomsen's work.

$$Co + Hg_2SO_4 = CoSO_4 + 2Hg \quad : \Delta H = 49,446$$

$$2Hg + SO_4 = HgSO_4 \quad : \Delta H = 175,000$$

$$Co + SO_4 = CoSO_4 \quad : \Delta H = 224,446$$

$$\text{I. C. T. value} \quad = 225,000$$

By taking the heat of formation of sulfuric acid as

880,000 kilojoules, and of 2HCl as 331,100 from International

Critical Tables; then following the convention that the heat

of formation of hydrogen shall be zero, we get on subtraction

of these values from those for the two salts above and taking

the average of the results the value given below for
heat of formation of the cobalt ion or for the reaction,

$$Co + 2H^+ = Co^{++} + H_2 \quad : \Delta H = 14,597 \text{ calories.}$$

THE FREE ENERGY OF SOLUTION OF COBALT CHLORIDE

One of the most difficult experimental problems
is the determination of the free energy change for a very
soluble salt going from the solid to hypothetical one
molal solution. In many cases it is possible neither to
set up a cell capable of giving the free energy change,
nor to use the Duhem equation for the lowering of the
freezing point of the solution, because of the inability
to obtain equilibrium between the anhydrous salt and the
solution.

If, however, there is available data for the
entropy of the ions and the heat of solution, as well as
entropy for the solid material an immediate calculation
of the free energy change may be made.

This may be illustrated for cobalt chloride.
Latimer (22) has shown that the entropy of many substances
in their compounds may be calculated from the equation

$$S_{298} = 3/2 \text{ R ln at. wt.} + So$$

where So = -.94. Applying this to cobalt and using the

mean value of the electromotive force for cobalt in one molal solution as found in this research to calculate the free energy change for the cobaltous potential, and from this the entropy for the aqueous ion there is obtained, by utilizing the heat of solution from the literature, the free energy change for solution of one mole of the salt in hypothetical one molal solution. The calculations follow:

CALCULATION OF THE FREE ENERGY OF SOLUTION OF
COBALT CHLORIDE

S_{298} = 3/2 R ln At. Wt. + So

$\quad$ = 3/2 x 1.9885 x 2.303 x 1.7704 - .94

$\quad$ = 11.32 calories per mole for cobalt in its compounds.

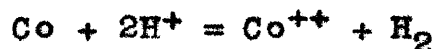Similarly Cl = 9.71 or 2Cl = 19.42 giving for solid $CoCl_2$

$$S_{298} = 30.74 \text{ calories}$$

The entropy of cobaltous ion may be obtained as follows:

$$\Delta F_{298} = -277 \times 2 \times \frac{96,496}{4.185} = -12,800 \text{ cals.}$$

$\Delta H \quad = -14,810$ cals.

$\Delta S \quad = -2,010/298 = -6.75$ cals.

$Co + 2H^+ = Co^{++} + H_2$

$7.2 + 0 \quad = x \quad + 29.44$

$\quad x = -28.95$ calories $= S_{298}$ for Co^{++}

Combining the above value with 2 Cl⁻ = 31 from
Latimer's data (loc. cit.) gives 2.05 cals, and this with
that for the solid gives ΔS = -28.69 for solution.

$\Delta F = \Delta H - T \Delta S$

$\quad = 18,410 - (-8,610)$

$\quad = 27,020$ calories per mole.

or remembering the convention that when heat is evolved it
has a negative value--

$\Delta F = -27,020$ cals.

CALCULATION OF THE ENTROPY OF SOLID COBALTOUS HYDROXIDE

By the utilization of the entropy of cobalt ion obtained from the electromotive force measurements we may, by suitable combination with other thermodynamic data, calculate the entropy of solid cobalt hydroxide, thus avoiding the difficulty of determinations of heat capacities at low temperatures. Very little is known concerning these values for the hydroxides, but we can calculate values which appear reasonable.

Taking $\triangle H$ as zero from Thomsen's measurements we have the problem of calculating the free energy change on solution. Almkvist (23) gives for the solubility of cobaltous hydroxide in water the value of 3.18 milligrams per liter at about $25^{\circ}C$. Taking the molecular weight as 92.94 and solving for the solubility product (assuming complete ionization) there results -

$$(3.422 \times 10^{-5}) \; (2 \times 3.422 \times 10^{-5})^2 = Ksp. = 1.6 \times 10^{-13}$$

Substituting this in the equation

$$nFE = RT \; 2.303 \; \log 1/1.6 \times 10^{-13}$$

$$= 1.9885 \times 298 \times 2.303 \times 12.7952$$

$$= 17,420 \; calories.$$

Now remembering that $\triangle F = -NFE$

and further that $\triangle F = \triangle H - T\triangle S$

and solving for ΔS

$$\Delta S = 58.4 \text{ cals per degree per mole.}$$

Taking $S_{OH^-} = -2$ and $S_{Co^{++}} = -28.95$

there is obtained for the entropy of solid cobaltous

hydroxide the value 25.45 calories per degree per mole.

CALCULATION OF THE EQUILIBRIUM CONSTANT

Postulating that at equilibrium $\triangle F = 0$ by definition we may use the equation

$$\triangle Fo = - RT \ln K$$

for the calculation of the equilibrium constant for the reaction taking place between cobalt and a solution of its ions. Thus taking $Eo = -\triangle F/nF$ and substituting on solving for K from the data -

$$.2777 = \frac{.05915}{2} \log K$$

$$\log K = 9.389 \text{ or } K = 2.449 \times 10^9$$

Replacement of Equilibrium (Solution Pressure)

For the reaction $1/2 \ Co + H^+ = 1/2 \ H + 1/2 \ Co^{++}$ $Eo = .2777$

Then
$$.2777 = .05915 \log K$$

$$= .05915 \log \frac{a_{Co}1/2 \ p_{H_2}1/2}{aH}$$

If the cobalt and hydrogen ions are at unit activity, we have

$$\text{Log } P = \log K \times 2 = 18.778$$

$$P = 5.998 \times 10^{18} \text{ atmospheres pressure}$$

to prevent the formation of hydrogen at the cobalt electrode.

DISCUSSION OF RESULTS

As previously mentioned all weights, volumetric apparatus, thermometers and the standard cell had been carefully calibrated. Hence errors arising from these or from the measuring apparatus are negligible.

From the temperature coefficient measurements the variation in temperature of the thermostat would produce a maximum deviation of about .0001 volts. The density measurements are very accurate, but the molality figures are less so, but would produce a change of no more than $\pm$ .0002 volts. Reference cells checked at all times more closely than this.

Although the materials were carefully purified, and impurities could not be detected in the cobalt sulfate, traces of iron and nickel were doubtless present although not in detectable amounts. Schildbach (loc. cit.) found that as much as 1% of nickel had no appreciable effect on the electrode potential.

It seems highly probable that oxygen and hydrogen were removed by the technique employed. However, it should be borne in mind that the electrode is exposed to the air for the second or two needed to transfer it from the filling vessel to the mercury seal with the reference electrode.

The form of the metal used here has shown again and again to be most likely to be free from strains and in its most stable state.

The assumption that cobalt salts behave as $MeSO_4$ and $MeCl_2$ seems warranted from previous work. However, here again it should be borne in mind that constancy of Eo is not necessarily a criteria for the validity of this, because degrees of ionization substituted for activities also give constant values.

Also, as mentioned hitherto, anodic and cathodic polarization as well as short circuiting produced only temporary disturbance, the equilibrium value being quickly regained. But a cell with an Eo value of .26 (18) behaved similarly.

Finally, it should be pointed out that the conditions of the determination, - - exactly duplicating the various steps in preparing each electrode - - should give reproducible results, although not necessarily the true value. Thus, hydrogen may have been present to the same extent each time or the influence of oxygen may have worked to the same extent, or adsorption of fuel gases, with their consequent partial removal to the same extent.

However, taking all these things into account we feel justified in assigning to the standard cobalt electrode the value $-.278 \pm .002$ volts at $25^{\circ}C$.

SUMMARY

1. The standard electrode potential of cobalt has been determined at 298.1, referred to hydrogen as zero, as $-.278 \pm .002$ volts.

2. The normal potential for the cobalt electrode has been determined as about $-.300$ volts.

3. The change in free energy for the reaction $Co + 2H^{++} = Co^{++} + H_2 = 12, 815$ calories.

4. The heat of reaction for this has been determined as 14, 597 calories.

5. The change in entropy from these two figures is determined as 5.98 calories.

6. $\Delta H, \Delta F, \Delta S, \Delta Cp, \bar{c}p$, have been determined for typical cells.

7. The free energy of solution of cobalt chloride has been determined as $-27,020$ calories.

8. The entropy of solid cobaltous hydroxide has been calculated as 25.45 calories per mole.

9. The equilibrium constant for the reaction $Co \rightleftharpoons Co^{++}$ has been calculated as 2.449×10^9.

10. It has been calculated for the reaction
$$1/2\ Co + H^+ = 1/2\ Co^{++} + 1/2\ H_2$$
that 5.998×10^{18} atmospheres would be needed to prevent the formation of hydrogen at the electrode.

11. The entropies of cobalt in its compounds, of
     cobalt gas ion, of cobaltous aqueous ion, and of
     solid cobalt chloride have been calculated as 11.32,
     37,86, -28.95 and 30.74 calories respectively.

12. The heats of formation of cobalt chloride and cobalt
     sulfate have been determined as 95,748 and 224,446
     calories respectively.

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